Sofia Alexandra Pereira Messias

Licenciada em Ciências da Engenharia Química e Bioquímica

Electrochemical Reduction of Carbon Dioxide dissolved in ionic liquids

Dissertação para obtenção do Grau de Mestre em Engenharia Química e Bioquímica

Orientador: Manuel Nunes da Ponte, Professor Catedrático, FCT/UNL
Co-orientador: Ana Reis Machado, PhD, Omnidea

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FACULDADE DE CIÊNCIAS E TECNOLOGIA
UNIVERSIDADE NOVA DE LISBOA

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MUITO OBRIGADO

Abstract

The present work studies a method of electrochemical reduction of CO_2 for the production of methane and methanol. Thus, a high pressure facility was assembled and tested for this goal. Some cyclic voltammetry experiments were carried out in order to study the electrochemical window of the electrolyte (the ionic liquid [bmim][BF_4] plus water). After the initial tests several electrolysis were performed with various electrode materials (copper, nickel, brass and carbon), at different pressures, reaction times and applied potential to study the influence of these parameters in the electrochemical reduction of CO_2. The principal product resulting from the electrochemical reduction of CO_2 was methane and hydrogen resulting from the electrolysis of water.

Keywords: Electrochemical Reduction; Carbon dioxide; cyclic voltammetry; Ionic liquids.

Resumo

O presente trabalho estuda um método para a redução eletroquímica de CO_2 para a produção de metano e de metanol. Assim, uma instalação de alta pressão foi montada e testada para esse objetivo. Algumas experiências de voltametria cíclica foram realizadas de forma a estudar a janela eletroquímica do eletrólito (líquido iónico [bmim][BF_4] mais água). Após os ensaios iniciais várias eletrólises foram realizadas com vários materiais como elétrodo (cobre, níquel, latão e carbono), a diferentes pressões, tempos de reação e potencial aplicado para estudar a influência destes parâmetros na redução eletroquímica de CO_2. O principal produto resultante da redução eletroquímica de CO_2 foi o metano e também se obteve hidrogênio resultante da eletrólise da água.

Palavras-chave: Redução eletroquímica; Dióxido de Carbono; Voltametria cíclica; líquidos iónicos.

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List of Symbols and Abbreviations

ILs – Ionic Liquids

[bmim][BF_4] – 1-Butyl-imidazolium-tetrafluoroborate

WE – Working Electrode

CE – Counter Electrode

RE – Reference Electrode

GC – Gas Chromatography

HS-GC – HeadSpace-Gas Chromatography

NMR – Nuclear Magnetic Resonance

1. Introduction

The growing concern with environmental problems, especially those related to carbon dioxide emissions has led to a growing demand for methods that reduce these emissions. Although it led to an increase of investment and development of low-carbon energy alternatives and renewable energies, predictions that the consumption of fossil fuels will grow significantly, due to increased global energy and electricity demand, caused by the emergence of new economic powers in the world. [1] One possible partial solution would be to chemically transform emitted carbon dioxide and recycle it as fuels or organic chemicals. [2]

The present work was carried out in the framework of a FP7 a research program that studies a method of electrochemical reduction of CO_2 for the production of methane and methanol. Thus, a high pressure facility was assembled and tested for this goal. Firstly some tests were performed to verify that the electrochemical cell was working properly, and some cyclic voltammetry experiments were also carried out in order to study the electrochemical window of the electrolyte. After the initial tests several electrolysis were performed, with various electrode materials, at different pressures, reaction times and applied potential, to study the influence of these parameters in the electrochemical reduction of CO_2. The different materials tested as working electrodes will be used as catalyst supports and/or catalyst supports. The information provided in this work will be used to develop further effective catalysts and cathodes for the electrochemical reduction of CO_2.

1.1. Carbon dioxide

Carbon dioxide is a colorless and inodorous gas with a low toxicity. Its solid form sublimes at 195 K, at atmospheric pressure.

Since the Industrial Revolution, greenhouse gas emissions, mostly CO_2, have been thrown into the atmosphere, due to the burning of fossil fuels. The increase of CO_2 in the atmosphere, which is claimed to be one the major contributors to the greenhouse effect, is expected to increase the temperature at the troposphere, the precipitation, and the sea level. Reducing these emissions has been recognized as essential in oreder to avoid potentially catastrophic climate changes [3].

1.1.1. Carbon dioxide capture

CO2 can be removed from the exhaust gases and then captured and stored in a place, preventing its release to the atmosphere. It can be sequestered by submersion in deep oceans, where it would be dissolved, or in aquifers very deep under the ground or sea, or in an oil and empty gas, or in disabled coal mines, as shown in Figure 1.1.

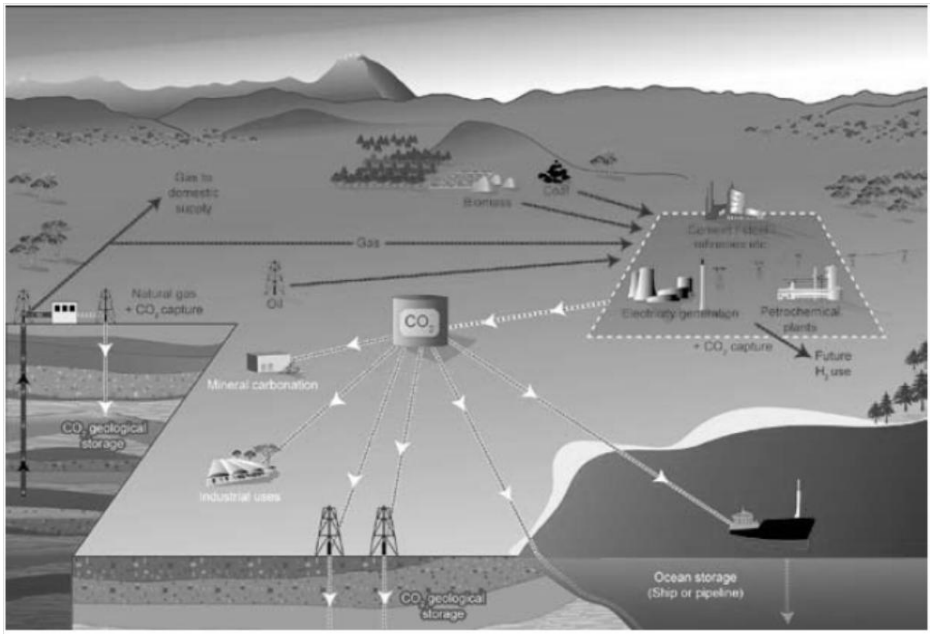


Figure 1.1 – Schematic diagram of possible CO2 capture and storage systems. Adapted [4]

The main purpose of CO2 capture is to produce a concentrated stream of CO_2 at high pressure that can readily be transported to a storage place. There are four basic systems for capturing CO_2 from the use of fossil fuels and/or biomass:

- Capture from industrial process streams: examples of the CO_2 capture from process streams are the purification of natural gas and the production of hydrogen-containing synthesis gas for the manufacture of ammonia, alcohols and synthetic liquid fuels. Most of the techniques are similar with those used in pre-combustion capture. [4]
- Pre-combustion capture: involves reacting to a fuel with oxygen or air and/or steam to give mainly a "synthesis gas" or "fuel gas" composed of carbon monoxide and hydrogen. The carbon monoxide is reacted with steam in a catalytic reactor, called a shift converter, to give CO_2 and more hydrogen. CO_2 is then separated, usually by a physical or chemical absorption process, resulting in a hydrogen-rich fuel which can be used in many applications. [4]
- Post-combustion capture: capture of CO_2 from flue gases produced by combustion of fossil fuels and biomass in air. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which separates most of the CO_2. The CO_2 is fed to a storage reservoir and the remaining flue gas is discharged to the atmosphere. [4]
  During the past years, absorptive post-combustion capture has become an emergent technique for greenhouse gas sequestration. The main reasons for the employment of absorptive post-combustion capture are the large scale availability, the very little impact on combustion/production process and CO_2 stream with high purity. The disadvantage of this concept is its high energy consumption. [5]
- Oxy-fuel combustion capture: nearly pure oxygen is used for combustion instead of air, resulting in a flue gas that is mainly CO_2 and H_2O. If fuel is burnt in pure oxygen, the flame temperature is excessively high, but CO_2 and/or H_2O-rich flue gas can be recycled to the combustor to moderate this. [4]

Figure 1.2 shows these systems in a simplified form.

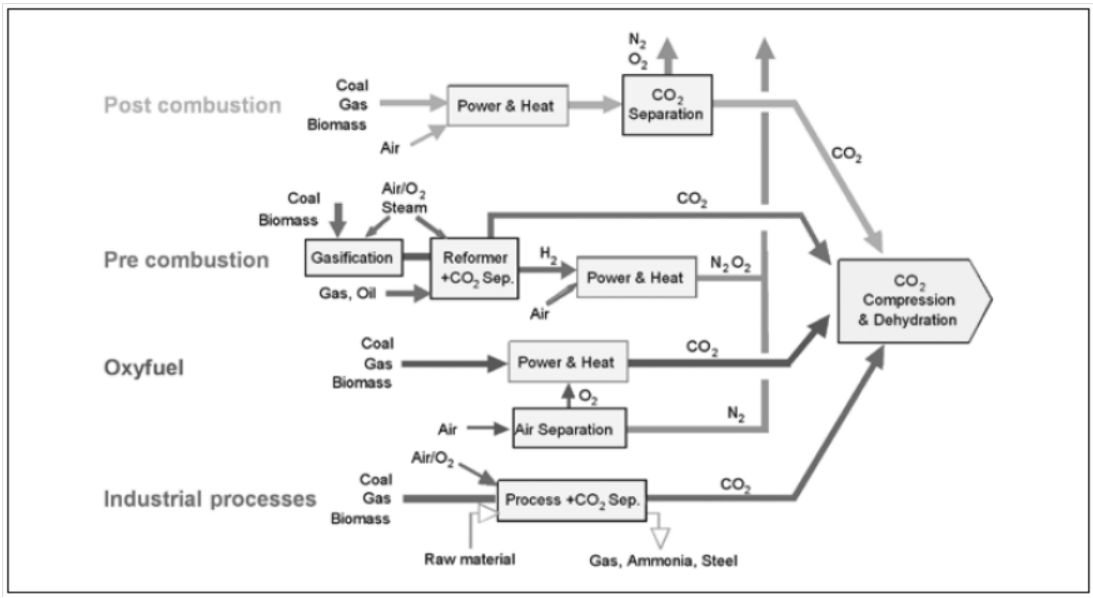


Figure 1.2 – CO_2 capture systems. Adapted [4]

1.1.2. Reduction of CO_2

The conversion and use of CO_2 is an important subject in modern chemistry, because CO_2 is an abundant, economical, non-toxic and recyclable carbon source [6]. Many methods can be used to convert CO_2 gas into fuels, for example photosynthesis, photocatalysis and electro-reduction [3]. Electro-reduction of CO_2 is believed to be one the most appropriate methods to convert CO_2 into organic compounds [7]. Electrochemical reduction of CO_2 gas may produce gases, such as methane, ethylene gases, as well as small organic molecules, such as formic acid and alcohols, [8] [3] as shown in Figure 1.3.

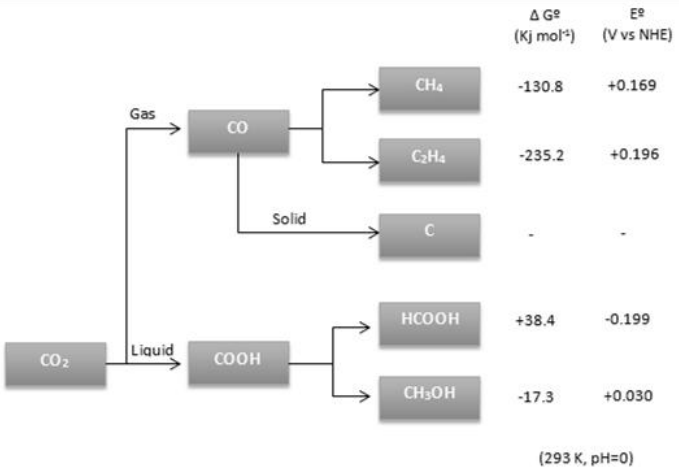


Figure 1.3 – Selected major reaction products and intermediates for CO_2 reductions with their associated free energies and standard potentials. Adapted [3]

Some of the reactions reported in the literature [8] [9] for the electrochemical reduction of CO_2 can be expressed as follows:

$$2CO_2 + 12H^+ + 12e^- \rightleftharpoons C_2H_4 + 4H_2O \quad (1)$$

$$CO_2 + 8H^+ + 8e^- \rightleftharpoons CH_4 + 2H_2O \quad (2)$$

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons CO + H_2O \quad (3)$$

$$CO_2 + 2H^+ + 2e^- \rightleftharpoons HCOOH \quad (4)$$

$$CO_2 + 6H^+ + 4e^- \rightleftharpoons CH_3OH + H_2O \quad (5)$$

The reactions correspond, respectively, to the formation of (1) ethylene, (2) methane, (3) carbon monoxide, (4) formic acid and (5) methanol.

1.2. Ionic liquids

Ionic liquids (ILs) are composed entirely of ions and exist in the liquid state below 100 ºC. As a class, ILs typically contains a bulky organic cation that is weakly coordinated to an organic or inorganic anion [10].

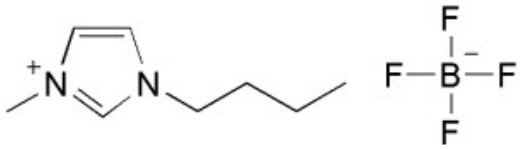


Figure 1.4 – Molecular structure of 1-Butyl-imidazolium-tetrafluoroborate

An increasing attention has been paid to the molten salts with melting points close to room temperature because they have many attractive properties: non-volatility, non-flammability, low vapor pressure, high conductivity. They are excellent solvents for both organic and inorganic substances and they are able to act as catalysts and wide electrochemical potential windows [7] [6] [11] [10]. The unique properties of ILs make them more environmentally attractive solvents; the ILs can replace the conventional toxic and volatile solvents [7] [6].

This work is related to the use of ILs as a solvent for electrochemistry. High conductivity and wide electrochemical windows make ILs very useful electrolytes with wide potential applications. ILs have been used in many electrochemical applications, as electrolytes in batteries, photo electrochemical cells, fuel cells and solvents in electrochemical experiments [7] [12] [10]. Another important aspect is the solubility of the CO_2 in ILs, previous studies found that the anion predominantly determines the solubility of CO_2 in ILs. ILs with fluorous anions, for example, bis(trifluoromethylsulfonyl)amide ($[Tf_2N^-]$), tetrafluoroborate ($[BF_4^-]$), and hexafluorophosphate ($[PF_6^-]$) show the highest CO_2 solubility. The solubility of CO_2 in an ILs is less strongly influenced by the type of the cation. However, the CO_2 solubility in ILs having fluorinated cations is higher than non-fluorinated cations. [13]

1.3. Electrochemistry

Electroanalytical techniques are related to the interaction between electricity and chemistry, i.e. in the relationship of chemical parameters with the electrical quantities as the potential, current or charge. Electroanalytical techniques have been used in many applications, such as environmental monitoring, industrial quality control, among others [14]

There are two main types of electroanalytical measurements: potentiometric and potentiostatic. In both cases the electrochemical cell should be composed of at least two electrodes (conductors) and a contact solution (electrolyte). These cells can be classified according to the consumption or production of energy, that is, when they consume electricity from an external source, they are classified as electrolytic: if they are used for the production of electrical energy, they are classified as galvanic. [14]

1.3.1. Cyclic voltammetry

In order to obtain qualitative and quantitative information on electrochemical reactions, cyclic voltammetry is generally the most used technique, as it provides quick and effective, information about the thermodynamics of redox processes, kinetics of electron transfer reactions in the electrode-solution interface, as well as the kinetics and mechanisms of chemical reactions initiated by heterogeneous electronic transfer. [14] [15]

Cyclic voltammetry is an electrochemical technique where it is possible to control the applied potential. By making a cyclical scanning of the potential, you can see what is the current produced, through the registration of current versus potential curves. These curves are made through a potentiostat system that will define the parameters of control. The aim is to impose a cyclic linear potential sweep on the working electrode and to output the resulting current-potential curve. This sweep is described in general by its initial (E_i), switching (E_s), final (E_f) potentials, and sweep (or scan) rate (v, in V/s). You can perform multiple cycles, but in most cases these will not be more informative than the single cycle. [14]

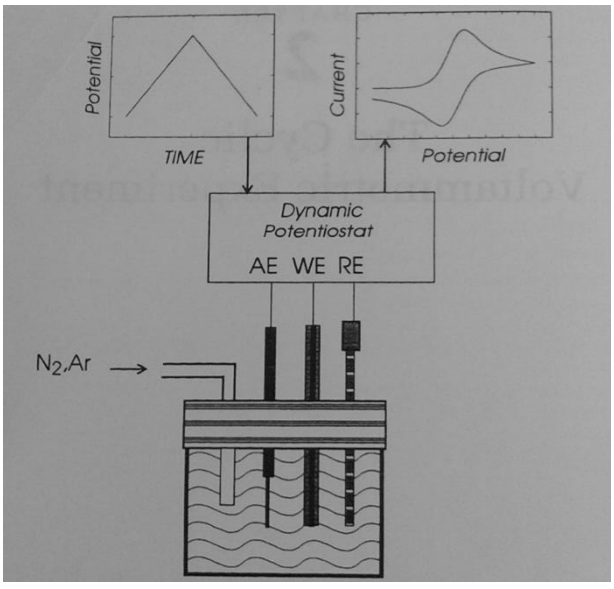


Figure 1.5 – Overall view of the cyclic voltammetry experiment. [14]

The electrochemical cell is usually made up of three electrodes, as shown in figure 1.5, the working electrode (WE), where the electrochemical reaction of interest occurs, an auxiliary electrode (AE) or “counter electrode” (CE) and a reference electrode (RE) and a solution (electrolyte) where the electrodes are immersed. The electrochemical reaction takes place because of the passage of an electrical current, also called faradic current, which is due to the electron transfer in WE. The potentiostat will operate the CE to balance the faradic process, with an electron transfer in the opposite direction, i.e., if the reduction takes place in WE the oxidation takes place at CE. Usually the processes that take place in CE are not of great interest and in most experiments the small currents observed mean that the electrolytic products formed in the CE do not influence the processes performed in WE. The faradic current in the WE is expressed by the output potential with a selected sensitivity, and is demonstrated in ampere per volt. [14]

There are still important aspects to be taken into account. At the beginning of the experiment, the cell contains solvent (electrolyte), one or more principal electroactive species, and possibly additional reagents that will be submitted to reactions with electrolytic products. Before starting the experiment it is necessary to remove the dissolved oxygen, which has a cathodic signal that can interfere with the observed current response. [14]

One of the aspects of great importance is the choice of solvent, where several factors must be taken into account, such as the conductance, the solubility of electrolyte and electroactive substance, and the reactivity with electrolytic products. [14] In recent years, ionic liquids have been studied as green solvents (electrolytes) in electrochemistry. Schröder and coworkers studied electrochemical properties of room temperature ionic liquids, BMMIMBF4, BMMIMPF6 and MDIMBF4 as solvents, using micro-samples, with a volume of 10 µl of ionic liquid under vacuum conditions and under conditions with controlled gas and moisture supplies. They studied the impact of water absorbed by the Ionic liquid in a controlled manner from the gas phase on the voltammetry of redox systems and ionic liquids potential window. The diffusion coefficients for three representative redox system, the oxidation of neutral N,N,N’,N’-tetramethyl-*p*-phenylenediamine (TMPD), the reduction of cationic methyl viologen (MV^{2+}) and reduction of anionic hexacyanoferrate(III), $Fe(CN)_6^{3-}$, were determined as a function of the water content of the ionic liquids. They have shown that traces of water can have a dramatic effect on the electrochemical characteristics and the rate of diffusion observed voltammetrically in ionic liquid media. In particular, the contrast in the effect of water on the diffusion coefficient for neutral and for ionic species suggests that wet ionic liquids may not be regarded as homogeneous solvents, but have to be considered as nano-structured with polar and non-polar regions. [16]

Barrosse-Antle et al. carried out voltammetry studies in room temperature ILs and compared them with conventional electrochemical solvents. Some surprising differences are reported. Room temperature ILs may offer significant advantages over their generally more volatile organic molecular solvent counterparts. For example, they often have high intrinsic conductivities (similar to aprotic solvents with added supporting electrolyte) resulting in simplified experimental arrangements. Many also have wide electrochemical windows (dictated by the high stability of the cation and anion) and this can allow additional voltammetric processes to be observed that are otherwise out of the potential range of traditional solvents. Apart from special classes (e.g., distillable), ionic liquids have a low volatility and high thermal stability, and may be used at elevated temperatures where they will not evaporate (in contrast to traditional volatile organic solvents). They also have the ability to solubilize a wide range of polar and nonpolar species. However, drawbacks include the high viscosity of RTILs (typically 2–3 orders of magnitude greater than conventional molecular solvents) resulting in small diffusion coefficients and slow voltammetric response times. In terms of their behavior as electrochemical solvents, in the majority of cases, mechanisms of electroactive species in RTILs

have been found to be similar to those reported in conventional solvents. The voltammetry is characterized by extremely slow rates of diffusion, and a decrease in the rate of heterogeneous electron transfer kinetics has been reported. The presence of a solute also may alter the double layer and hence background current more frequently than occurs in molecular solvents with added electrolyte. As a result of these findings, it may be appropriate to assume that RTILs do not behave in a fully analogous manner to traditional molecular solvents with bulk added supporting electrolyte but that they should be treated as a separate class of solvent. [17]

1.3.2. Electrolysis

Electrolysis is the process in which electrical energy is used to force the occurrence of a chemical reaction that is not spontaneous. [18]

The physical-chemist Michael Faraday (1791-1867) studied quantitative aspects of electrolysis conducting various experiments. Through these experiments, he concluded that the mass of product formed (or the consumed reagent) in an electrode is proportional to the quantity of electricity transferred at the electrode and the molar mass of the substance, i.e. the higher the intensity of the electrical current in electrolysis, the bigger the mass of the formed product. [18] The electric charge is defined by the following expression:

$$Q = i.\Delta t$$

Where i is the intensity of the electric current (the SI unit is the ampere (A), defined as coulomb per second (C/s)) and Δt is the time interval.

In 1909, the American physicist Robert Andrews Millikan (1868-1953) determined the amount of charge carried by a mole of electrons, called Faraday constant, which has a value of 96500 C (1F). [18] Therefore, by knowing the amount of charge provided in electrolysis, it is possible to predict the amount of substance that is produced in this process. It is possible to set the 1st and 2nd Faraday's law.

1st Faraday's law – the mass that forms in an electrode is directly proportional to the amount of charge flowing through the circuit. This law is expressed by the following equation: [19]

$$m = K_1.Q$$

Where m is the mass of the substance produced, k_1 is the constant of proportionality and Q the electrical charge in C.

2nd Faraday's law - The mass of different substances liberated by the same quantity of electric charge is proportional to their chemical equivalents. This law is expressed by the following equation: [19]

$$m \propto E$$

Where m is the mass of substance produced and E is the chemical equivalent that is the mass that an element loses or gains in mole of electrons.

Faradaic efficiency (FE) - Describes the efficiency with which a charge is transferred in a system, in order to facilitate the electrochemical reaction. The faradaic efficiency for the reduction products depend remarkably upon electrode potential, temperature, electrolyte, concentration of electrolyte, purity of electrode material. [20]

Faradaic efficiency is calculated using the theoretical charge of the substance i (Q_T (i)), and the total charge passed (ΣQ_p), through the following expression. [7]

$$FE(i)(\%) = \frac{Q_T(i)}{\sum Q_p} \times 100$$

1.4. State of the Art

In recent years, several researchers have been studying the electrochemical reduction of CO2, initially using aqueous solutions and later using organic solvents. Hori et al. studied the electroreduction of CO2 at Cu in aqueous inorganic electrolytes and verified that the CO is formed as an intermediate from the CO2, being adsorbed on the copper electrode where is then reduced to hydrocarbons and alcohols. [21] Hara et al. studied the electrochemical reduction of carbon dioxide under high pressure on various electrodes in an aqueous electrolyte. They found that the main products on Ag, Au, Zn, Pb and In electrodes were formic acid and/or CO, as at CO_2 pressure of 1 atm. On group 8 -10 metals, such as Fe, Co, Rh, Ni, Pd and Pt, the main reduction products were formic acid and/or Co under high pressure. [22]

Saeki and coworkers studied the electrochemical reduction of CO_2 with high current density in a CO_2+methanol medium, at various metal electrodes; they verify that the most electrodes gave the same main product in this system an in aqueous system. At W, Ti an Pt electrodes, CO_2 reduction was inefficient. Sn and Pb electrodes were active in formate production. However, CO was formed much more efficiently in this system than in the aqueous system. Hydrocarbon formation at Cu electrode was less efficient when compared with aqueous system, but in the Ni electrode hydrocarbon was formed efficiently. [23]

Kaneco et al. investigated the electrochemical reduction of high pressure CO_2 at a Cu electrode in cold methanol and found that the main products formed were methane, ethylene, carbon monoxide and formic acid. In the electrolysis of high pressure CO_2 at low temperature, the reduction products were formed in the order of carbon monoxide, methane, formic acid and ethylene. [24]

Due to the excellent proprieties of ionic liquids as electrolytes and as solvents for CO_2 in recent years, the first studies using ionic liquids for electrochemical reduction of CO_2 have appeared. Zhao and coworkers investigated the electrochemical reduction of CO_2 in ionic liquid; they use 1-N-butyl-3-methylimidazolium hexafluorophsphate as a solvent and electrolyte, supercritical CO_2, and water were successfully electrolyzed, and the products were CO, H_2 and small amount of formic acid. [7]

Feng et al. studied a Nanoporous copper incorporated platinum composites for electrocatalytic reduction of CO2 in ionic liquid [bmim][BF_4]. The electrochemical behavior of this electrode for electrocatalytic reduction CO2 in ionic liquid, had been studied by cyclic voltammogram and electrochemical impedance spectroscopy with a reduction peak at −2.24 V (vs. Ag) which was more positive 180 mV than that obtained on a pure platinum electrode. The electrolyses experiments were carried out in an undivided cell under mild conditions without any toxic solvents, catalysts and supporting electrolytes, affording the dimethyl carbonate in a good yield (81%). [6]

Further studies have been made in different ionic liquids such as Laura Barrosse-Antle and Richard Compton who studied the CO_2 reduction in 1-butyl-3-methylimidazolium acetate. Where CO_2 was reduced via a chemically irreversible, one electron transfer to the radical anion $CO_2^{-\bullet}$ at -1.3 V versus Cc^+/Cc. Probable follow-up chemistry includes the formation of oxalate, carbon monoxide and carbonate, so mineralizing the CO_2. [25]

Another study was carried out by Snuffin et al. investigated the catalytic electrochemical reduction of CO_2 in ionic liquid $EMIMBF_3Cl$. A novel ionic liquid $EMIMBF_3Cl$ that contains a BF_3Cl^- anion has been synthesized. This is the first report of an ionic liquid with a BF3Cl- anion. It was found that CO_2 gas can be dissolved and electrochemically reduced at ambient pressure, and room temperature in the ionic liquid $EMIMBF_3Cl$. The reduction of CO_2 occurred at a relatively less negative electrode potential of -1.8 V versus silver wire, compared to previous reported values that are between -2.4 and -2.0 V. The reduction current density can be as high as an approximately 5.7 mA/cm^2. The BF_3Cl^- anion may catalyze the CO_2 reduction by forming a Lewis acid-base adduct BF_3^-CO2. [26]

2. Experimental Method

2.1. Reagents and Materials

Carbon dioxide and Argon were supplied by Air Liquid with a stated purity of 99.98%.

The copper foil and nickel foil working electrodes used were supplied by Alfa Aesar. The materials has the following characteristics, copper foil: 0.5 mm (0.02 in) thick, puratronic 99.998% (metals basis), oxygen free around 11.2g/50x50mm; nickel foil: 1.0mm (0.04 in) thick, 99.5% (metals basis), oxygen free around 22.3g/50x50mm. Copper foam was purchased from Metafoam technologies ref. Cu std MP-004. Its porosity was 89.2% and the pore size was 550 µm. A commercial alloy 67% copper, 33% zinc microstructured in the form of a foil 1mm of thickness was also used as working electrode. A carbon cloth type B1 was purchased from Clean Fuel Cell Energy Lt. and tested as working electrode. A commercial zinc foil 0.05mm of thickness was used as sacrificial electrode. A silver rod with a purity > 99% was used as quasi-reference electrode.

The ionic liquid [bmim][BF_4] it was synthesized by the Solchemar.

2.2. Description of the high pressure facility

The high pressure facility used, as shown in figure 2.1, can be divided in three sectors: The reaction sector, the expansion sector and the sampling sector. This pressure facility is operated in batch mode. The reaction sector consists in one 150 cm^3 stainless steel reactor placed inside one insulated box (thermostatic air bath), where the heating is provided by an infrared lamp and the temperature is controlled by a temperature controller (Fluke 2100, Hart scientific). The reactor is equipped with a pressure controlled (Omron K3JT by OMRON corporation) and ¼ tubing for gas inlet and discharge of the gaseous reaction mixture into the expansion zone. Electric connections of the electrodes go through one 10 mm stainless tube with a conax pressure fitting. Outside the reactor the electric wires are connected to a potenciostat. Inside the stainless steel reactor there is a glass beaker. The electrolyte is placed in this beaker together with a magnetic stirring bar and the electrodes are immersed in the electrolyte. The expansion and sampling sectors lie outside the air bath. The stainless steel expansion vessel has a volume of 150 cm^3 and the stainless steel sampling vessel has a volume of 50 cm^3.

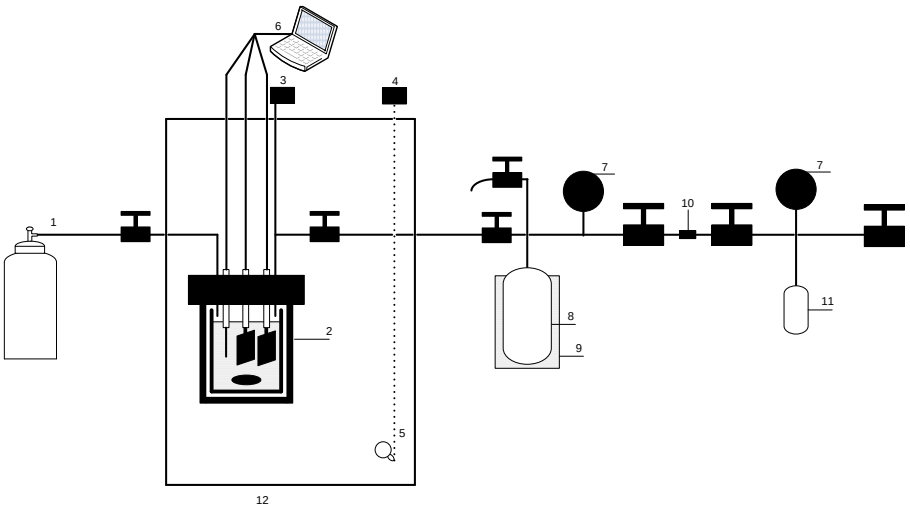


Figure 2.1 - High pressure facility; (1) CO_2 inlet; (2) Reactor with electrochemical cell; (3) Digital Pressure Meter; (4) Digital Temperature Meter; (5) Infrared lamp; (6) Potentiostat; (7) Pressure Meter; (8) Expansion zone vessel; (9) cooling mixture; (10) Nut; (11) Smpling vessel; (12) Insulated box

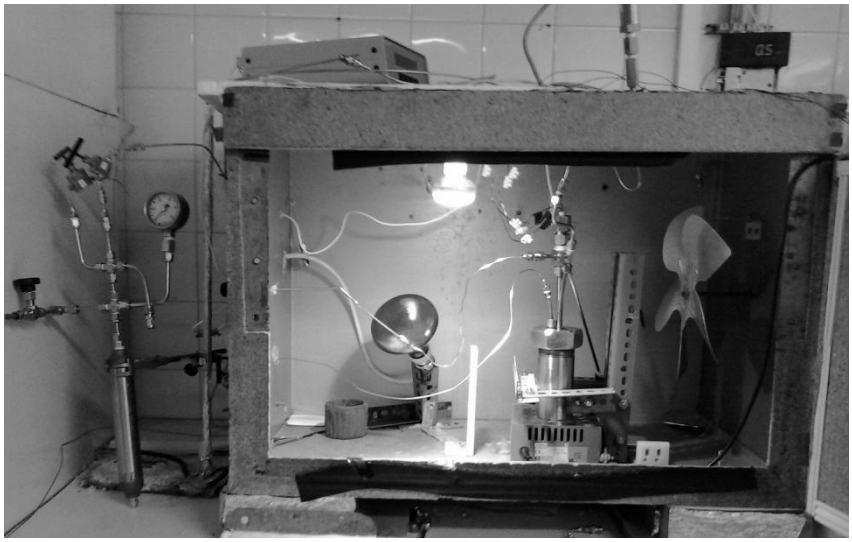


Figure 2.2 – High pressure facility

2.3. Calibration Procedure

The calibration is very important because we need to know the volume occupied by the gas in different areas to be able to quantify the process. The calibration was performed using the following procedure

First of all, a calibrated vessel was assembled as shown in figure 2.3, 2.5 and 2.6. The calibrated vessel valves are opened and the temperature is let to stabilize. Argon is introduced with a pressure less than 2.5 bar. When the pressure was stable it was measured using a precision Keller manometer and all valves are closed. Then the area to be calibrated is evacuated. Next, the vaccum pump is turned off and the pressure is measured. Finally the valves of the calibration vessel are opened and the pressure is measured when it stabilizes. The calibrated volume of the facility is calculated through the ratio pressure values.

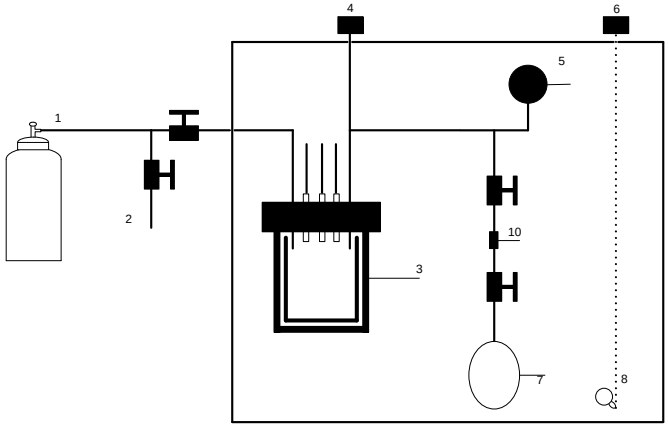


Figure 2.3 - Calibration of High Pressure facility, reactor sector; (1) Argon inlet; (2) Argon output and vacuum line; (3) Reactor; (4) Digital Pressure Meter; (5) Precision Digital Pressure Meter; (6) Digital Temperature Meter; (7) Calibration vessel; (8) Infrared lamp; (9) Box; (10) Nut

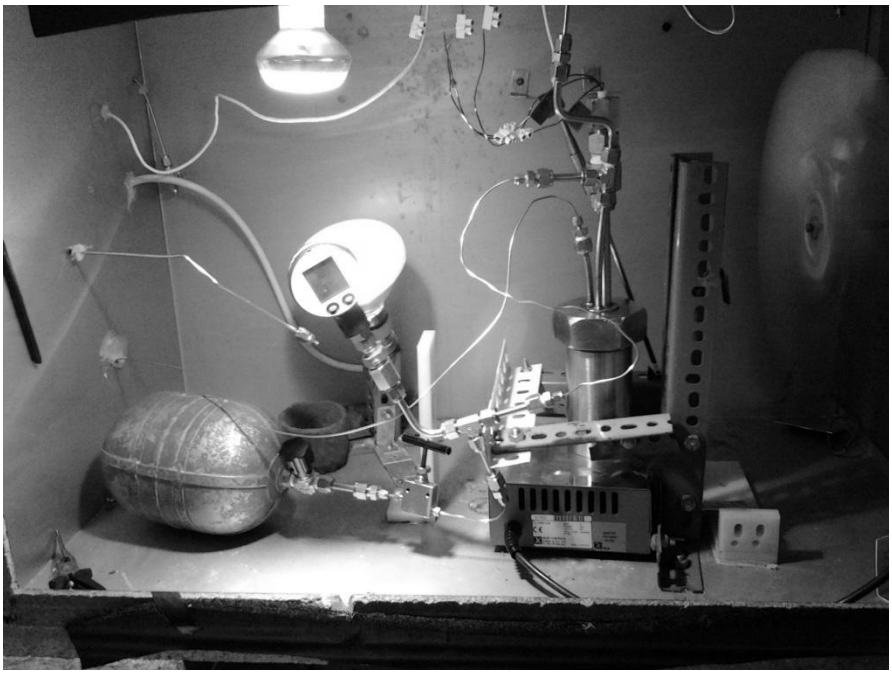


Figure 2.4 – Calibration of High Pressure facility, reactor sector.

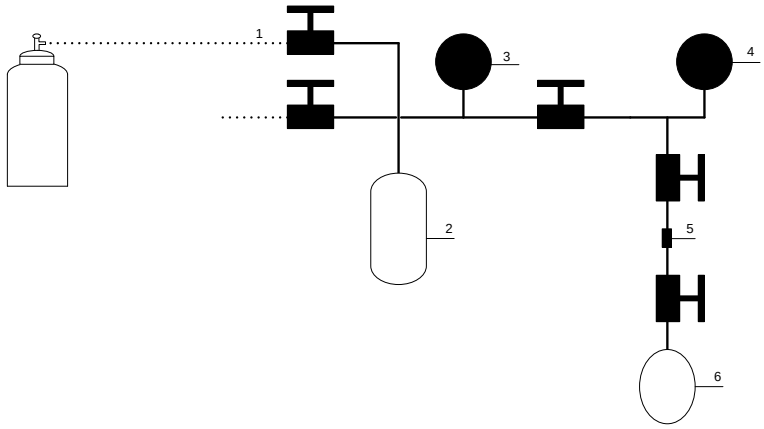


Figure 2.5 - Calibration of Expansion vessel; (1) Argon inlet, output and vacuum line; (2) Expansion vessel; (3) Pressure Meter; (4) Precision Digital Pressure Meter; (5) Nut; (6) Calibration balloon

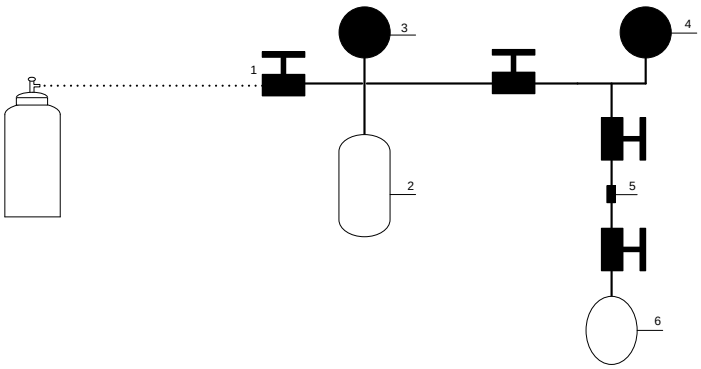


Figure 2.6 - Calibration of Collecting vessel; (1) Argon inlet, output and vacuum line; (2) Collecting vessel; (3) Pressure Meter; (4) Precision Digital Pressure Meter; (5) Nut; (6) Calibration balloon

2.4. Electrolysis Procedure

The Electrolysis was carried out according to the following procedure:

First of all, the electrochemical cell was assembled, Figure 2.7 shows a schematic representation of the electrochemical cell. The cell was sealed and, at the same time, the three electrodes were immersed into IL. After the reactor was connected to the facility, CO_2 was charged into the cell up to 30 bar, and then the reactor was purged at least three times, to remove the oxygen in the system. When the temperature of the air bath and the pressure of the cell stabilizes at the desired values for the experiment the power source is turned on and the electrolysis is carried out with the programme "*CONTROL*" as a function of square wave, where the working pulses duration is 900 seconds and the cleaning pulses 10 seconds. The power source was built by Omnidea Lda.

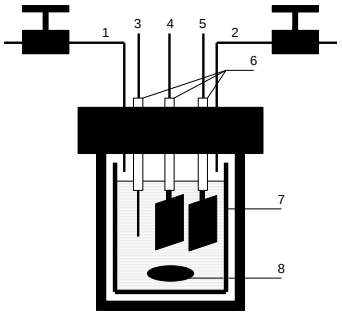


Figure 2.7 - Structure of the high-pressure electrochemical cell: (1) gas inlet; (2) gas out; (3) quasi-reference electrode; (4) cathode: working electrode; (5) anode: counter electrode; (6) Teflon packing; (7) glass beaker; (8) stirrer. Adapted [7]

After running the program, it is necessary to make vacuum in the expansion zone. The valve at the entrance of this zone is opened, keeping the reactor outlet valve closed. When the pressure is the same in reactor and in the expansion zone, sampling collecting vessel is connected to the expansion zone vessel and the sampling zone is evacuated. The expansion vessel is placed in a cooling mixture of water, salt and N_2 liquid, and the pressure goes down and stabilizes. After the pressure stabilizes the valve which connects the sampling vessel and the expansion zone vessel is connected, until the pressure in the manometer is 2 bar. Finally the sampling vessel is disconnected and is ready for GC analysis.

2.5. Electrochemical Characterization by Cyclic Voltammetry

The Cyclic Voltammetry was made according to the following procedure:

First of all, the electrochemical cell was assembled, Figure 2.7 shows a schematic representation of the electrochemical cell. The cell was sealed and, at the same time, the three electrodes were immersed into IL. After the reactor was connected to the facility CO_2 was charged into the cell up to 30 bar, and then the reactor was purged at least three times remove the oxygen in the system. When the temperature of the air bath and the pressure of the cell stabilizes at the desired values for the experiment the power source is turned on and the cyclic voltammetry is carried out with the programme "*NOVA*" with a scan rate of 20 mV/s. The power source was AUTOLAB 84469.

2.6. Water control (Karl Fischer)

Karl Fischer titration is a classic method in analytical chemistry, which uses coulometric or volumetric titration to determine quantities of water in a sample. In this work, this technique was used to check the amount of water present in ionic liquid [bmim][BF_4] (electrolyte) before and after the reaction. In all electrolysis experiments the same quantity of water was added. The water content of the electrolyte samples analyzed before the reactions was in the range of 16-19%.

2.7. Analytical methods (GC and Headspace)

Gas products were collected in a collection vessel and analyzed by gas chromatography. An Agilent Micro GC 3000 was used equipped with a backflush 1 µl injector. The separation of the compounds present in the gas current was done in two columns. One of the columns was a MolSieve 5A 10 m x 0.32 mm with Plot U 3 m x 0.32 mm pre-column, with argon as carrier gas (Channel 1). The other column is a Plot U 8 m x 0.32 mm column with a Plot Q 1 m x 0.32 mm pre-column with helium as carrier gas (Channel 2). After separation on the column the sample gas flows through a thermal conductivity detector (TCD). On channel 1 is possible to observe the peaks relating to inorganic compounds and methane, on channel 2 it is possible to observe the peaks to heavier compounds and CO_2.

The micro GC instrument conditions is: Injector temperature at 90ºC for both Channels; Column temperature at 100ºC and 60ºC for channel 1 and 2 respectively; Sampling time is 10s for both channels; Injection time for channel 1 and 2 is 200ms; Run time is 180s to the channel 1 and 2; Column pressure 30psi and Pressure equilibration time is 10s for both channels; For channel 1 the Post-run pressure is 40psi and for channel 2 is 32psi; Detectos sensitivity is standard to channel 1 and High to channel 2; Detector data rate is 50Hz, Baseline off set is 0mV and Backflush time is 9.5s for the two Channels.

The qualitative identification of the products in the ionic liquid [bmim]BF_4 was carried out by a TRACE GC Ultra Headspace. The carrier gas used first is the Helium (1.5ml/min) and after changed to Hydrogen (1ml/min) and the oven program used was 50ºC (1min) to 130ºC (2min) at 10ºC/min. The column used was a 100% Dimethyl Polysiloxane (dimensions: 30mx0.32mm I.D. column coated with a 3.0 µm thickness film.

Figure 2.8 – Headspace Gas Chromatography

2.8. Spectroscopic methods (NMR)

The spectroscopic method used to identify the products in the ionic liquid was the nuclear magnetic resonance (NMR). The analyses were performed on the Bruker Avance III 400, with a frequence of 400mHz.

3. Results and Discussion

3.1. Electro-reduction of CO_2

In this chapter the influence of working electrode composition, CO_2 pressure voltage applied and electrolysis time in the electrochemical reduction of CO_2 using the ionic liquid [bmim][BF_4] with 16-19% water as electrolyte and zinc as an sacrificial anode will be studied.

The calculated values for concentrations of methane and hydrogen presented must be considered with care, as the calculation were based in a single concentration (one point calibration). Thus, for concentrations that are considerably different from the calibration concentration, the estimated concentration may be a very rough estimation involving a significant error (10%).

3.1.1. Copper electrode

3.1.1.1. Voltammetry

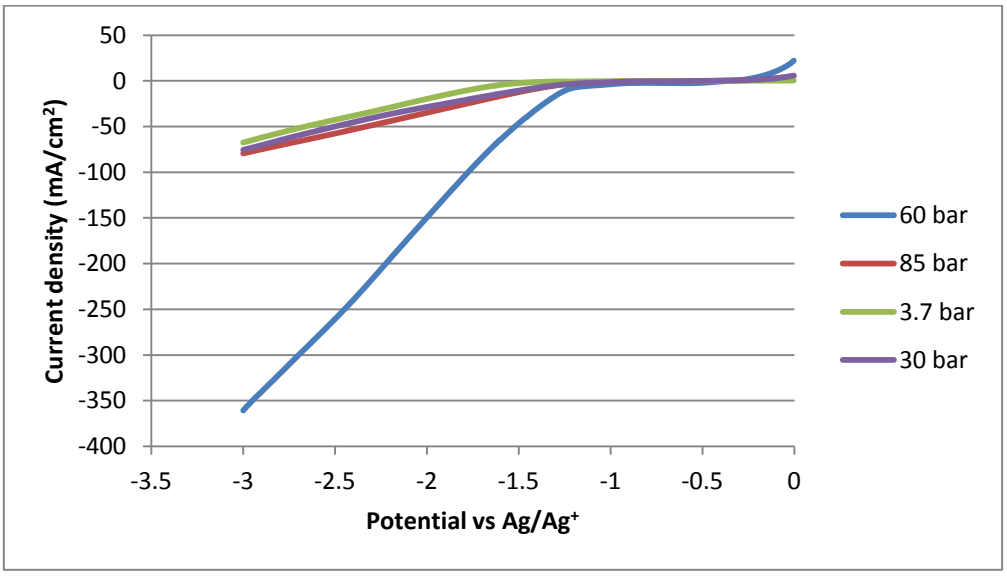


Figure 3.1 – Cathodic Curve 1st cycle with scan rate of 20 mV/s

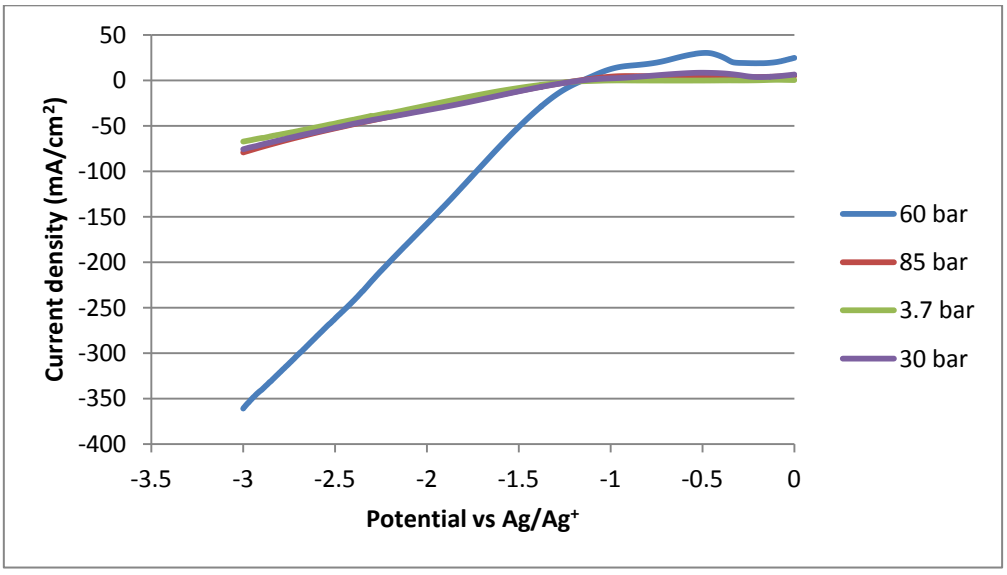


Figure 3.2 - Anodic Curve 1st cycle with scan rate of 20 mV/s

Figure 3.1 shows the cathodic curve at the Cu electrode in ionic liquid [bmim][BF_4] with 16-19% water as electrolyte, it was measured at 318 K and at different pressures. Argon was used as reference at a pressure of 3.7 bar, CO_2 was used for the other pressures. Comparing the voltammetric curves at different pressures with the reference pressure, it is observed that the highest currents are obtained for the electrolysis carried out at 60 bar. This may be explained by equilibrium between CO_2 inflow to the electrode and less sites available for hydrogen adsorption. The current starts to increase at a potential of -1.3 V vs Ag/Ag^+ quasi-reference electrode. For the other pressures, currents of the same order of magnitude as for argon were obtained.

Figure 3.2 shows the anodic curve of the same electrode in the same conditions, and it is possible to observe an oxidation wave at 60 bar pressure. No oxidation waves are observed at the other pressures.

3.1.1.2. Analysis of the gas phase

Electrolysis experiments were carried out as described in the experimental section 2.6. Electrolysis were performed potentiostatically and under stirring in the conditions presented in table 3.1.The analysis of the gas phase was done by GC as described in the experimental section. The chromatograms are presented in Annex 3.

Table 3.1 – Reactions performed with copper electrode and GC results

Reaction	WE	CE	Applied Potential (V) vs. Ag/Ag^+	Conditions	Detection	Concentration (ppm)
1	Cu (2 cm^2)	Zn	-1.8	Pressure: 60 bar Temperature: 45ºC Time: 1 hour	CH_4 H_2	CH_4: 889 H_2: 2655
2	Cu (1.7 cm^2)	Zn	-1.8	Pressure: 66.5 bar Temperature: 45ºC Time: 30 minutes	CH_4 H_2	CH_4: 996 H_2: 2673
3	Cu foam (1.2 cm^2)	Zn	-1.8	Pressure: 64.5 bar Temperature: 45ºC Time: 13 minutes	CH_4 H_2	CH_4: 4832 H_2: 19601
4	Cu (2.1 cm^2)	Zn	-1.8	Pressure: 85 bar Temperature: 45ºC Time: 30 minutes	CH_4 H_2	CH_4: 1624 H_2: 2321
5	Cu (1.8 cm^2)	Zn	-1.3	Pressure: 66.3 bar Temperature: 45ºC Time: 30 minutes	CH_4 H_2	CH_4: Traces H_2: 1588
6	Cu (cm^2)	Zn	-0.5	Pressure: 63.1 bar Temperature: 45ºC Time: 30 minutes	H_2	H_2: 387

According to the data presented in table 3.1, methane starts to be produced significantly at voltages higher than -1.3 V vs Ag/Ag^+ at 60 bar pressure. At the same pressure at -0.5 V vs Ag/Ag^+ no CO_2 reduction products were detected. Comparing for example the methane concentrations obtained in reaction 2 and 4 it can be verified that an increase in pressure increases significantly the concentration of methane in the reaction mixture and consequently the yields of methane. The best result for methane conversion in the conditions studied was obtained when a Cu foam was used, even with the shortest experiment time. This type of structure has a larger surface area (much higher than the electrode nominal area).

3.1.1.3. Analysis of the liquid phase

Some samples of the liquid phase (electrolyte) were analyzed by headspace-chromatography. Figure 3.3 shows the headspace chromatogram of a blank sample (ionic liquid

plus water). The observed increase in the base line in the chromatograms is due to the water present in the ionic liquid. This is a serious drawback of this analysis method because compounds with boiling points close to the boiling point of water (such as formic acid) cannot be detected as they co-elute with the water present in the sample.

In the chromatogram of the electrolyte after reaction 1 with Cu (2 cm^2), shown in figure 3.4, it is possible to observe a peak at 6.09 minutes, in the case of the reaction 2 with Cu (1.7 cm^2), shown in figure 3.5, no peaks other than the peaks of the blanks are observed.

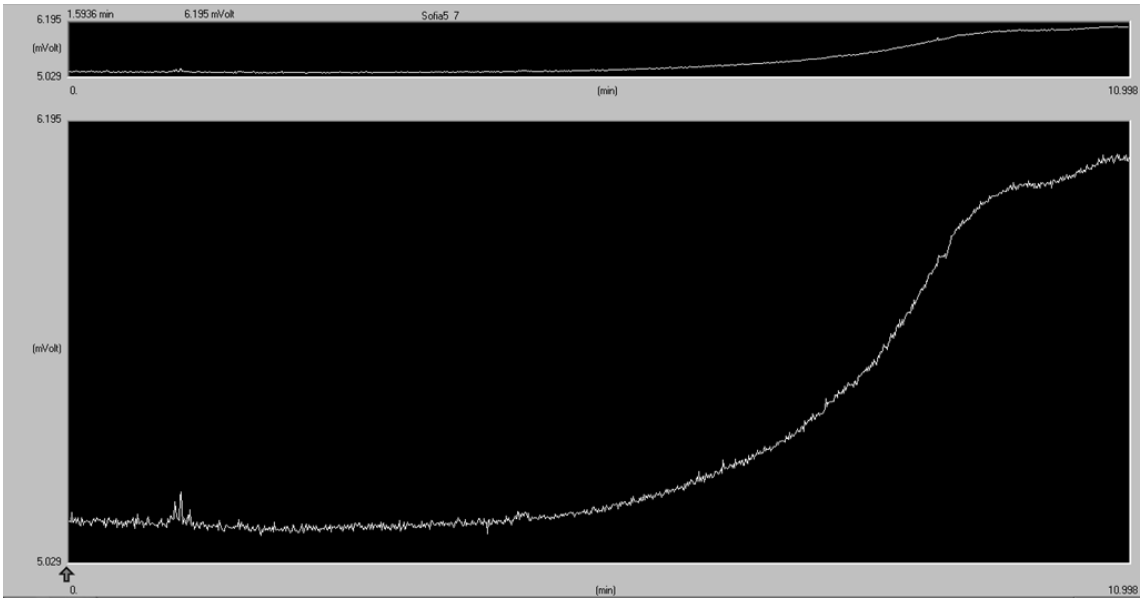


Figure 3.3 – Headspace gas chromatogram of blank sample (ionic liquid plus water)

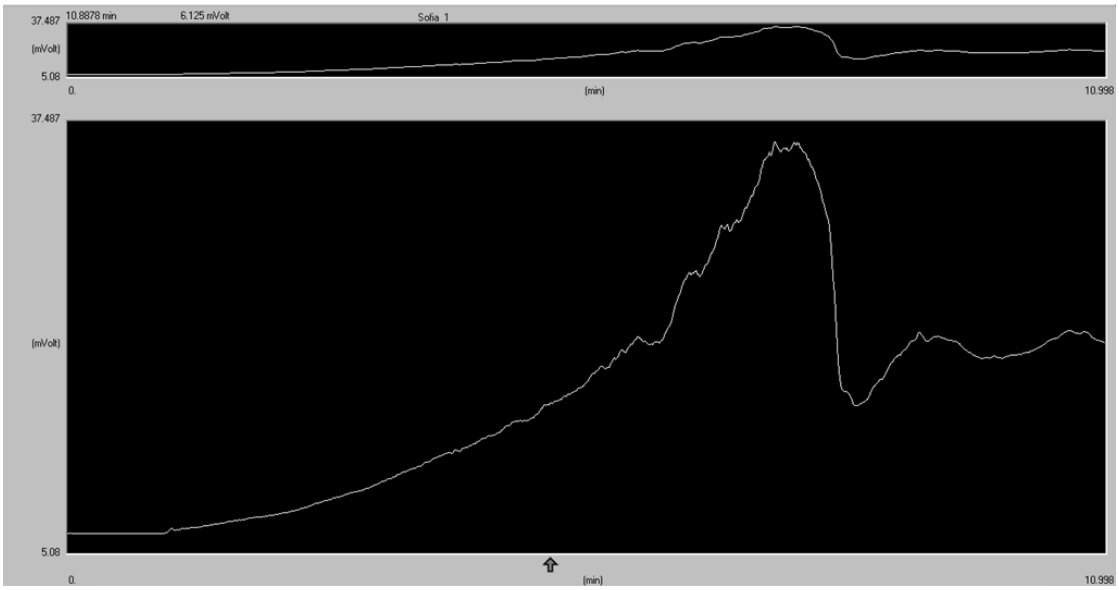


Figure 3.4 – Headspace gas chromatogram of CO_2 electrolysis carried out with an applied potential of -1.8V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 60 bar and 1 hour reaction time (reaction 1)

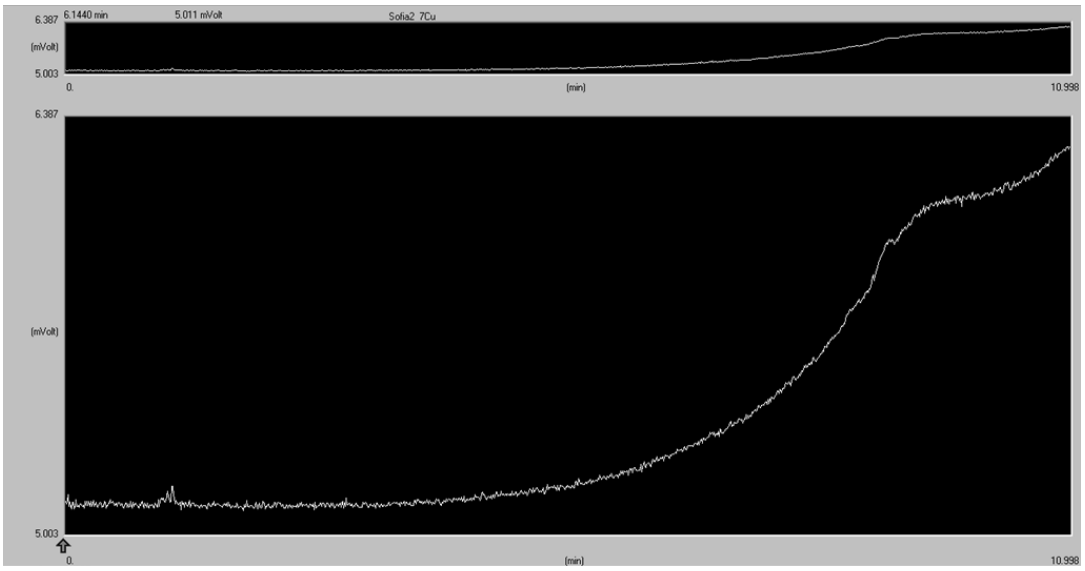


Figure 3.5 - Headspace gas chromatogram of CO_2 electrolysis carried out with an applied potential of -1.8V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 66.5 bar and 30 minutes reaction time (reaction 2)

The results do not allow us to conclude which compounds are present in the sample, ^{1}HNMR spectroscopy of some samples was performed. As the solvent used in the reactions was the IL [bmim] [BF4], it is important to first identify the peaks corresponding to the protons of the IL. In order to facilitate the analysis was assigned a number to each proton.

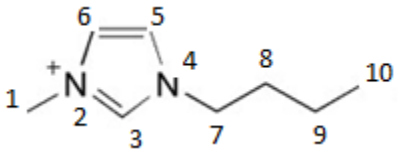


Figure 3.6 – Molecular structure of $[bmim]^+$

The ^{1}HNMR spectrum of the ionic liquid [bmim][BF_4] exhibts a triplet at 0.9, which corresponds to number 10 protons. The next peaks, at 1.3 and 1.8 are a sextet and a quintet, and correspond to number 9 and 8 protons respectively. The peak with a chemical shift at 4 ppm is a singlet and corresponds to proton 1. The peak following the 4.2 signal is a triplet and corresponds to number 7 protons. Between 7 and 9 ppm the peaks corresponding to the aromatic ring can be observed. The peaks corresponding to number 5 and 6 protons are very close to each other, are both singlet (we can say that is a duplet) with values around 7.5 ppm. The last peak with a sign around 8.8 ppm corresponds to number 3 proton.

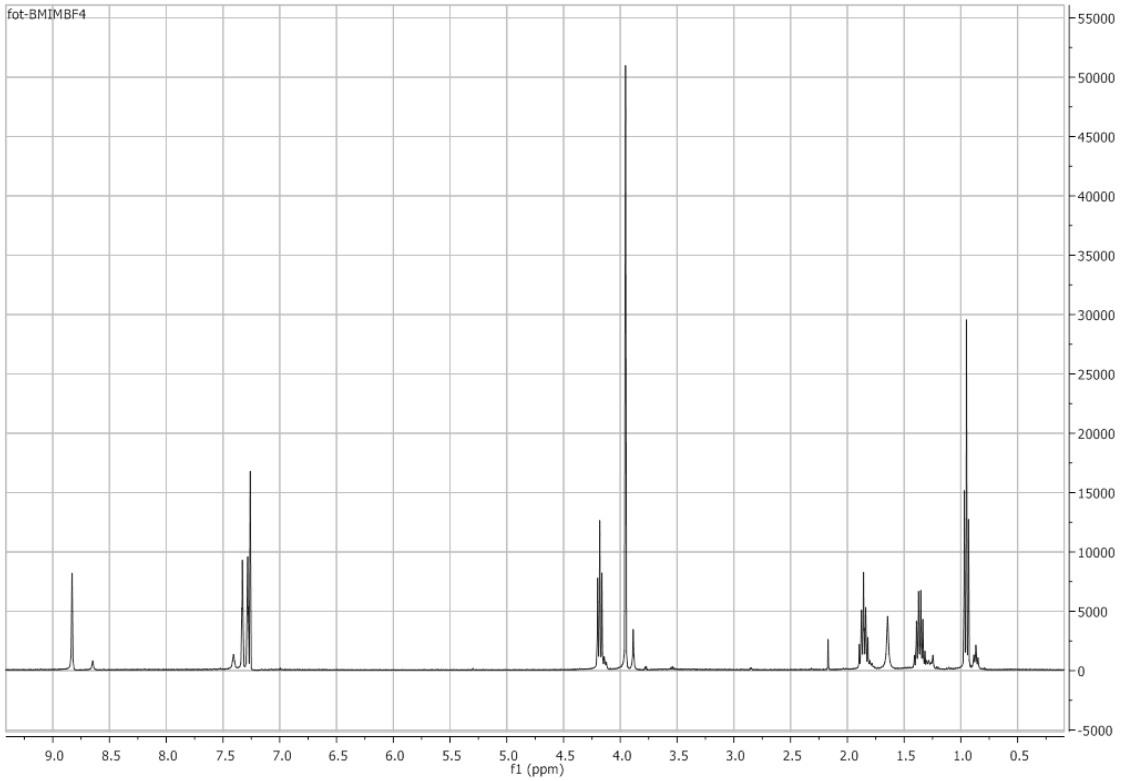


Figure 3.7 - Proton NMR spectrum of the ionic liquid [bmim][BF_4]

The solvent used to perform the NMR was deuterated chloroform, the peak corresponding to the proton of this solvent is a singlet at 7.26 ppm. The sample contains water and has a peak at 1.5ppm, which is a singlet assigned to the water protons. The peak that appears in all of the samples at 2.2 ppm was assigned to the acetone used in the washings of the NMR tubes.

From the NMR spectrum of figure 3.8, it was possible to identify the peaks corresponding to the Ionic Liquid, solvent used $CDCl_3$, water and acetone used in the washing of the NMR tubes, but besides these peaks more peaks are observed in figure 3.8. These peaks are:

δ = 2.9 (s); δ = 3.8 (s); δ = 4.75 (s); δ = 8.7 (s).

The peaks that appear in the range of 2-3 ppm, might be assigned to acids formed during the reduction of CO_2, such as formic acid. The peak at 3.8 ppm may be assigned to methanol. Fulmer at al., assigned the signal at 3.42 ppm to methanol when $CDCl_3$ is used as a solvent. [27] To confirm these assumptions additional tests will be carried out.

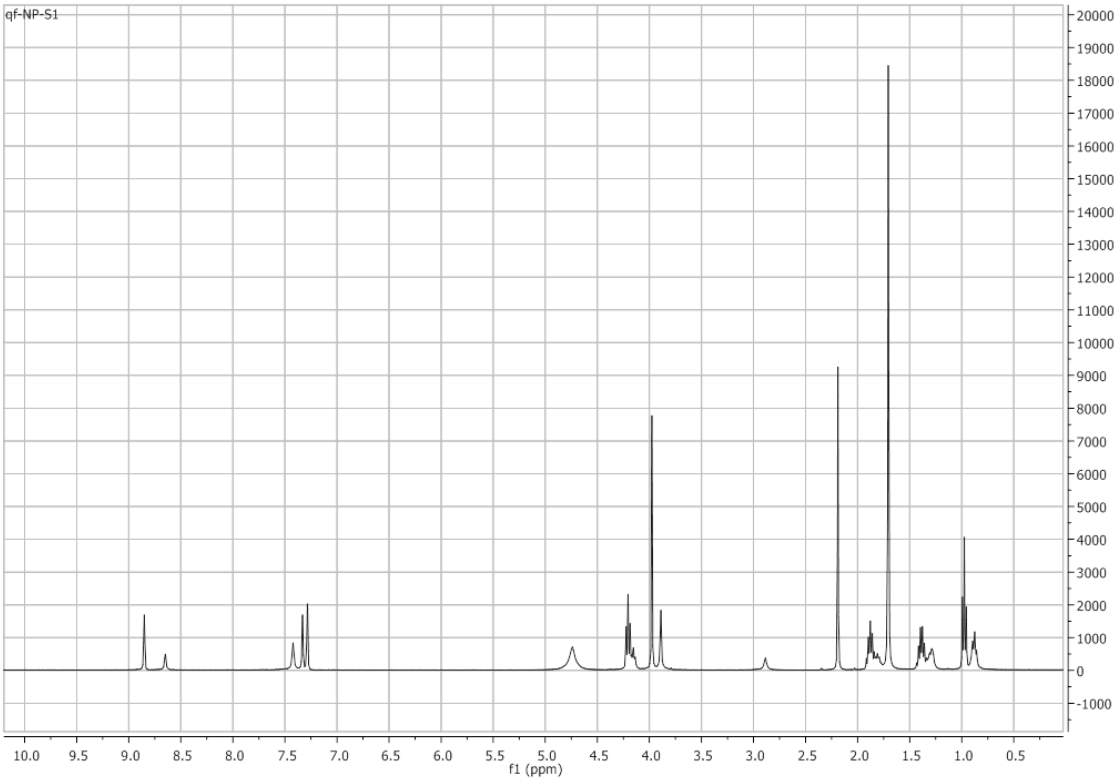


Figure 3.8 – Proton NMR spectrum of the electrolyte of the electrolysis carried out with an applied potential of -1.8V vs Ag/Ag^+, at a temperature of 45ºC, at a pressure of 60 bar and 1 hour reaction time (reaction 1).

3.1.2. Nickel electrode

3.1.2.1. Voltammetry

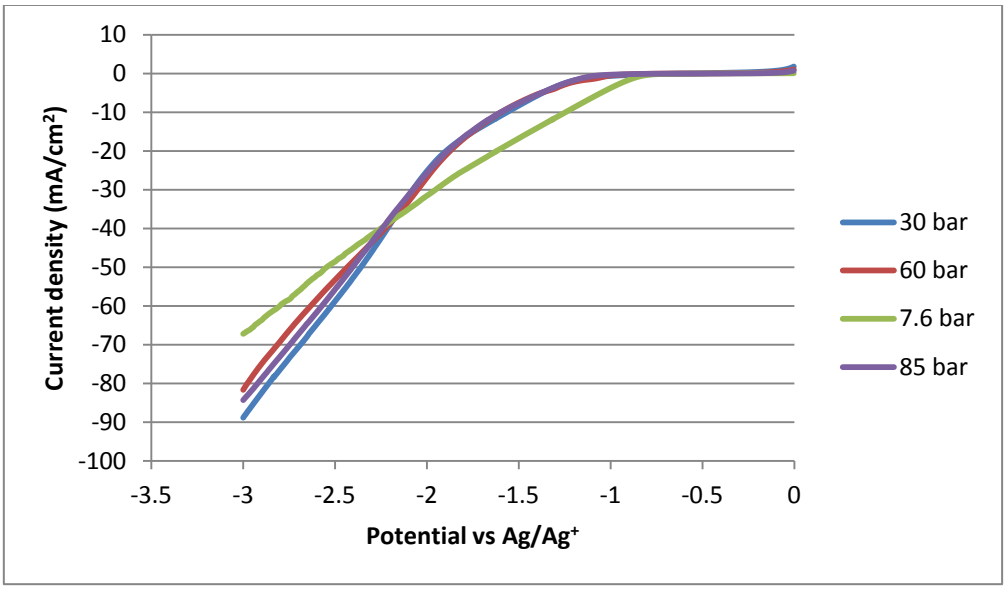


Figure 3.9 - Cathodic Curve 1st cycle with scan rate of 20 mV/s

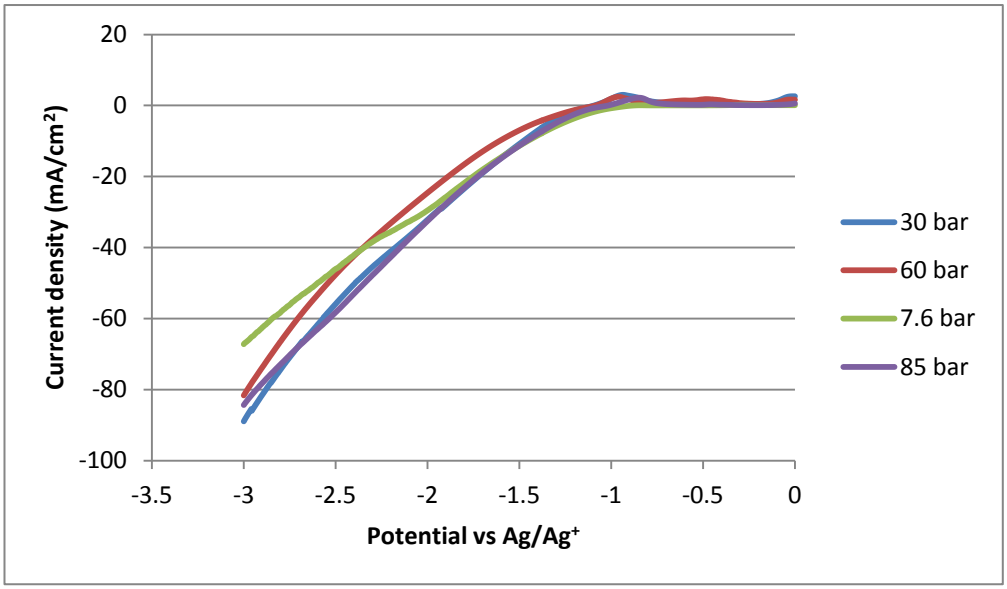


Figure 3.10 - Anodic Curve 1st cycle with scan rate of 20 mV/s

Figure 3.9 shows the cathodic curve at the Ni electrode in ionic liquid [bmim][BF_4] with 16-19% water as electrolyte, it was measured at 318 K and at different pressures. Argon was used as reference with a pressure 7.6 bar, CO_2 was used for the other pressures. In this the currents on Ni are practically the same for the three pressures studied, the onset potential was around -1.2 V vs. Ag/Ag^+ for the 30 bar, 60 bar and 85 bar pressures, but it is possible to observe a decrease in current between the potential -1V and -2.4V vs. Ag/Ag^+ when compared with the reaction carried out in argon. For applied potentials more negative than -2.4 V vs. Ag/Ag^+ the currents for the reactions in CO_2 are higher than in argon.

Figure 3.10 shows the anodic curve of the same electrode in the same conditions, and the curves of the three pressures are very similar, as all have the oxidation wave for an applied potential of -1V vs. Ag/Ag^+.

3.1.2.2. Analysis of the gas phase

Electrolysis experiments were carried out using [bmim][BF_4] with 16-19% water as electrolyte as described in the experimental section 2.6. Electrolysis were performed potentiostatically and under stirring in the conditions described in Table 3.2. The analysis of the gas phase was done by GC. The chromatograms are presented in Annex 4.

Table 3.2 – Reactions conditions performed with nickel electrode and GC results

Reaction	WE	CE	Applied Potential (V) vs. Ag/Ag^+	Conditions	Detection	Concentration (ppm)
7	Ni (2.1 cm^2)	Zn	-2.4	Pressure: 86 bar Temperature: 45ºC Time: 3 hours	CH_4 H_2	CH_4: 2276 H_2: outside of the calibration zone
8	Ni (1.8 cm^2)	Zn	-1.8	Pressure: 85.5 bar Temperature: 45ºC Time: 1 hour	CH_4 H_2	CH_4:641 H_2: 606
9	Ni (2.4 cm^2)	Zn	-1.6	Pressure: 85.3 bar Temperature: 45ºC Time: 1 hour	CH_4 H_2	CH_4: traces H_2: 1877
10	Ni (1.8 cm^2)	Zn	-1.8	Pressure: 61.1 bar Temperature: 45ºC Time: 1 hour	CH_4 H_2	CH_4: 1771.5 H_2: 5027

Methane was the only gaseous CO_2 reduction product detected. The largest methane production was obtained at the potential of -2.4 V vs. Ag/Ag^+. This result could be expected from the analysis of the cathodic curve for the Ni electrode.

Contrary to what could be expected, the concentration of methane in reaction 8 at higher pressure is lower than the concentration of methane in reaction 10. This experiment will be repeated to confirm this result.

3.1.2.3. Analysis of the liquid phase

Some samples of the liquid phase (electrolyte) were analysed by headspace-chromatography. In the chromatogram of the electrolyte after reaction 7 with Ni (2.1 cm^2), no peaks other than the blank can be observed. In the case of reaction 8 shown in figure 3.12 it is possible to observe a peak at 6.45 minutes and one peak in the beginning of the chromatogram assigned to a column impurity.

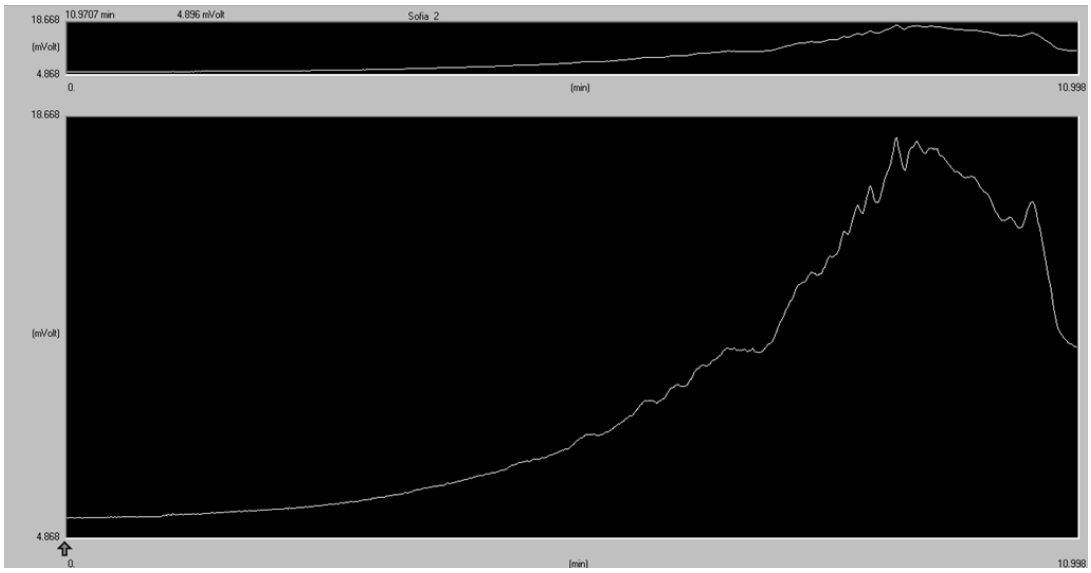


Figure 3.11 - Headspace gas chromatogram of CO_2 electrolysis carried out with an applied potential of -2.4V vs. Ag/Ag^+, at a temperature of the 45ºC, at a pressure of 86 bar and 3 hours reaction time (reaction 7).

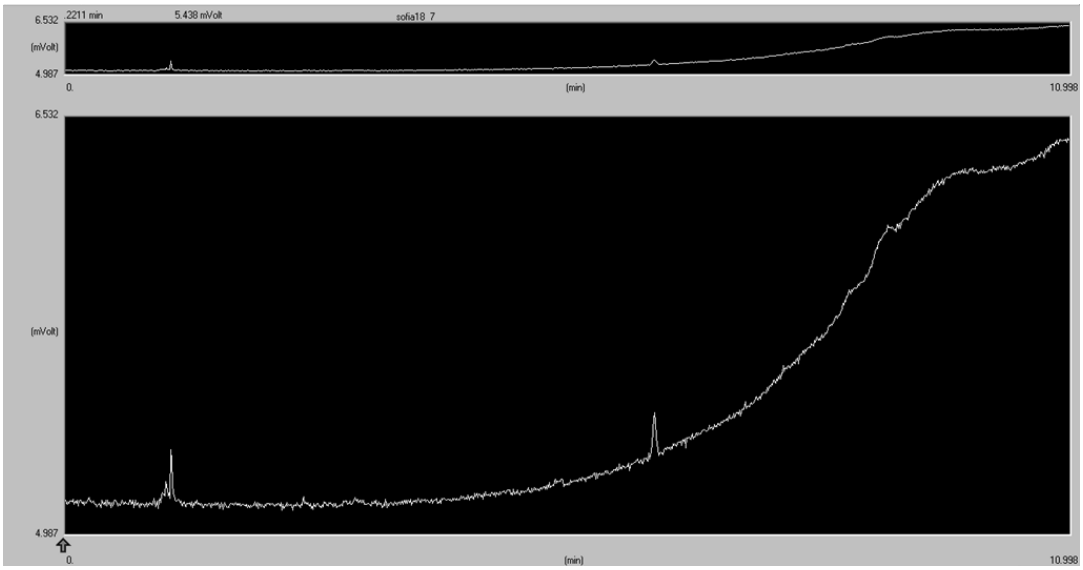


Figure 3.12 - Headspace gas chromatogram of CO_2 electrolysis carried out with at an applied potential of -1.8V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85.5 bar and 1 hour reaction time (reaction 8).

As happened with copper, this results do not allow us to conclude which are the compounds present in the sample, so an ^{1}HNMR spectroscopy was performed.

In the NMR spectra represented below, it is possible to identify the following peaks:

- Peaks assigned to the IL: δ = 8.8 (1H,s,3); δ = 7.4 (1H,s,5); δ = 7.3 (1H,s,6); δ = 4.2 (2H, t,J=6Hz,7); δ = 4 (3H, s,1); δ = 1.8 (2H, mult,8); δ = 1.3 (2H, mult,9); δ = 0.9 (3H, t,J=6Hz,10);
- Peaks assigned to the $CDCl_3$: 7,26 (1H,s)
- Peaks assigned to the H_2O: 1,52 (2H,s)
- Peaks assigned to the acetone: 2.2 (s)

In the figure 3.13 are still observed the following peaks:

δ = 4.75 – 5.75.

and in the figure 3.14:

δ = 2.8 (s); δ = 3.8 (s); δ = 8.6 (s).

As has already been mentioned above, the peaks that lie in the range 2-3 ppm may be assigned to acids formed during the reaction and the peak at 3.8 ppm may be assigned to the methanol. Additional analysis will be carried out to confirm these assumptions.

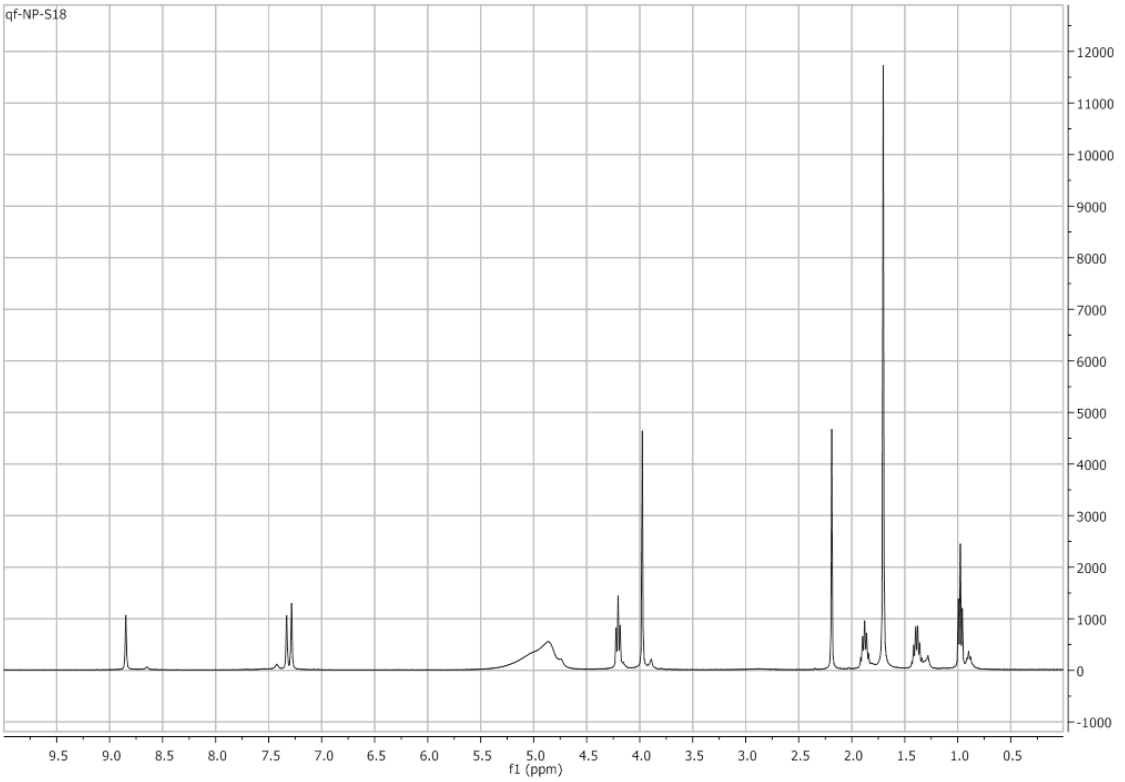


Figure 3.13 - Proton NMR spectrum of the electrolyte of the electrolysis carried out with an applied potential of -1.8V vs. Ag/Ag^{+}, at a temperature of 45ºC, at a pressure of 85.5 bar and 1 hour reaction time (reaction 8)

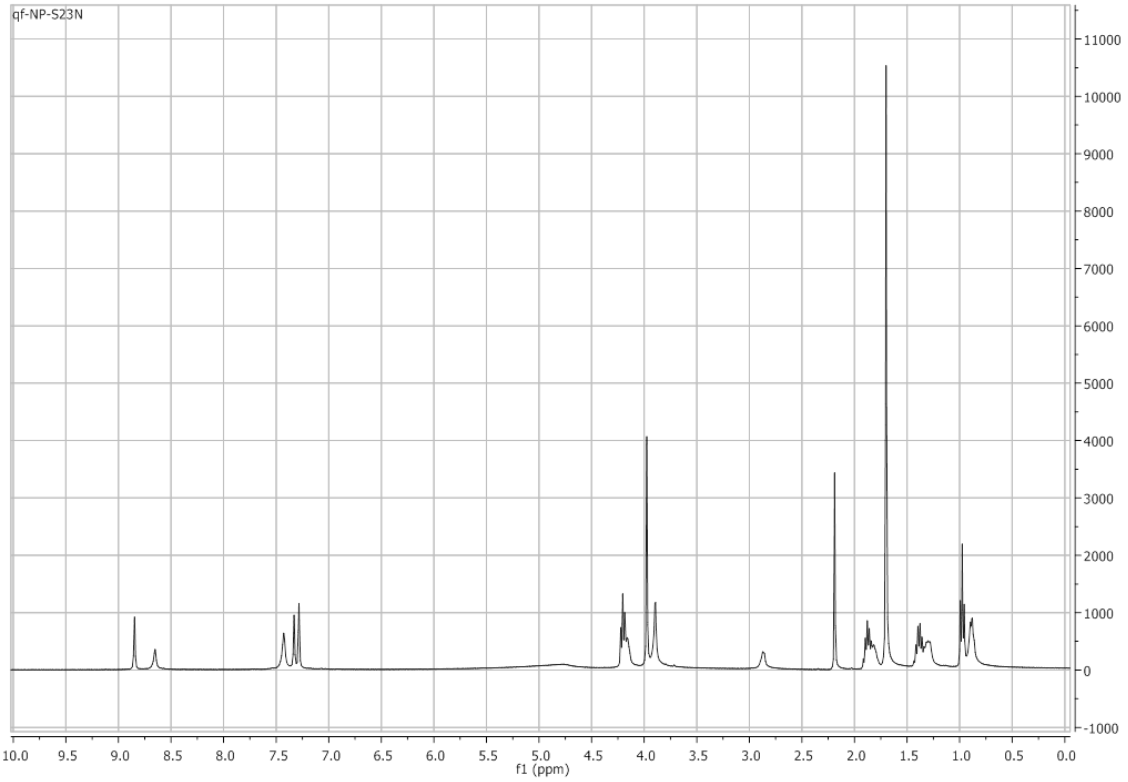


Figure 3.14 - Proton NMR spectrum of the electrolyte of the electrolysis carried out with at an applied potential of -1.6V vs. Ag/Ag^{+}, at a temperature of 45ºC, at a pressure of 85.3 bar and 1 hour reaction time (reaction 9)

3.1.3. Brass electrode

3.1.3.1. Voltammetry

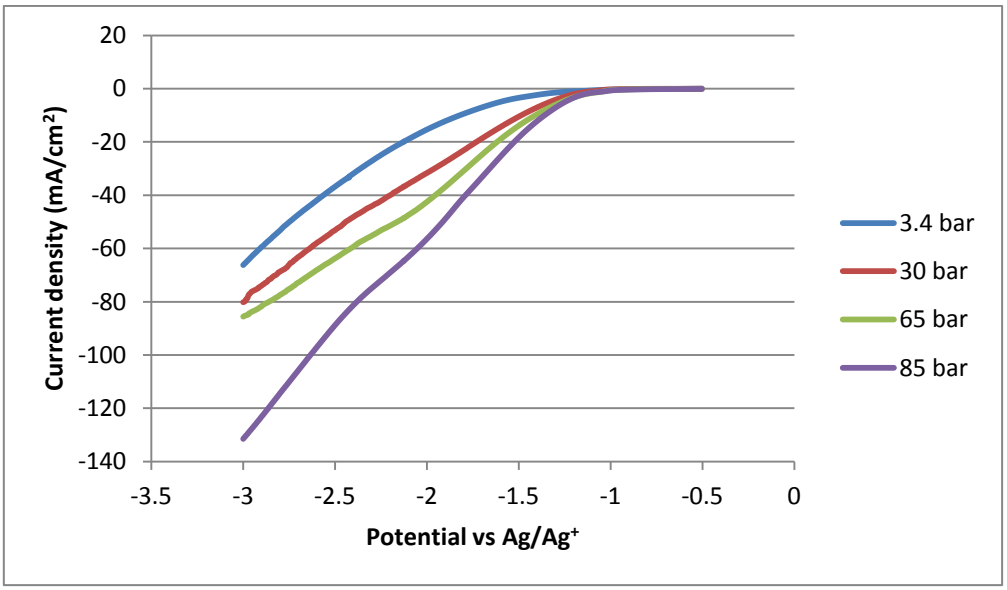


Figure 3.15 - Cathodic Curve 1st cycle with scan rate of 20 mV/s

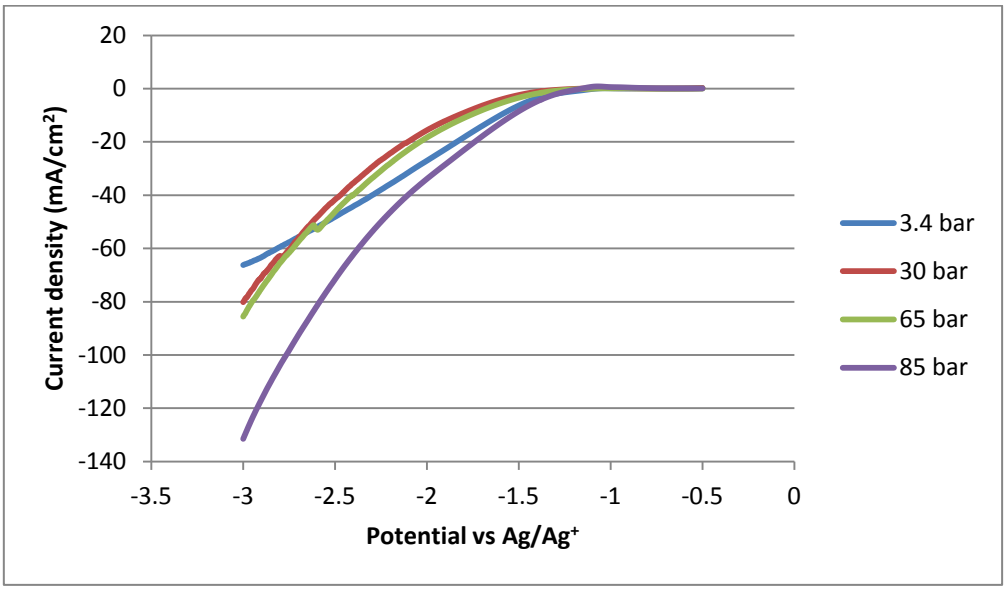


Figure 3.16 – Anodic Curve 1st cycle with scan rate of 20 mV/s

Figure 3.15 shows the cathodic curve at the brass electrode in ionic liquid [bmim][BF_4] with 16-19% water as electrolyte, it was measured at 318 K and at different pressures. Argon was used as reference at a pressure of 3.4 bar, CO_2 was used for the other pressures. Observing figure 3.15 it turns out that current increases with increasing CO_2 pressure. The curve for the pressure of 85 bar is the one that differs most from the reference curve. For all the pressures the onset potential for current increase was around -1.2 V vs.Ag/Ag^+.

Figure 3.16 shows the anodic curve of the same electrode in the same conditions, it is observed that there aren't oxidation waves for any of the pressures.

3.1.3.2. Analysis of the gas phase

Electrolysis experiments were carried out using [bmim][BF_4] with 16-19% water as electrolyte as described in the experimental section 2.6. Electrolysis was performed potentiostatically and under stirring. The analysis of the gas phase was done by GC. The chromatograms can be observed in Annex 5.

Table 3.3 – Reactions conditions performed with brass electrodes and GC results

Reaction	WE	CE	Applied Potential (V) vs. Ag/Ag^+	Conditions	Detection	Concentration (ppm)
11	Brass (1.7 cm^2)	Zn	-2.4	Pressure: 63.3 bar Temperature: 45ºC Time: 2 hours	CH_4 H_2	CH_4: 5502 H_2: 41053
12	Brass (1.7 cm^2)	Zn	-1.8	Pressure: 62.9 bar Temperature: 45ºC Time: 30 minutes	CH_4 H_2	CH_4: 2128 H_2: 1858

In the case experimental conditions of reaction 11 methane and another unidentified gaseous product were detected (see channel 2 chromatogram in annex 5 reaction 11). This additional CO_2 reduction product appears with retention times close to hydrocarbons with two carbon atoms, such as ethylene and ethane. Additional experiments must be carried out to confirm the formation and to identify a possible second CO_2 gaseous reduction product.

Also additional electrolysis conditions are necessary to characterize the behavior of brass towards CO_2 electrochemical reduction.

3.1.3.3. Analysis of the liquid phase

A sample of the electrolyte after reaction 12 with Brass (1.7 cm^2), was analysed by headspace chromatography and the chromatogram is shown in figure 3.17. It is possible to observe a peak at 2.19 minutes.

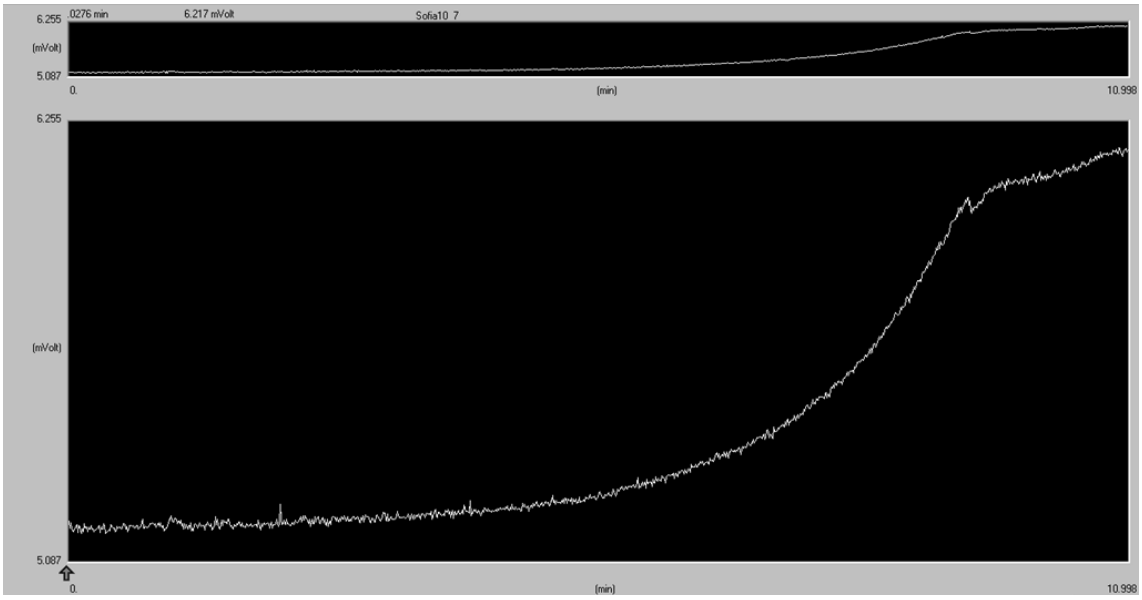


Figure 3.17 - Headspace gas chromatogram of CO_2 electrolysis carried out with an applied potential of -1.8V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 62.9 bar and 30 minutes reaction time (reaction 12).

Again, the results do not allow us to conclude which are the compounds present in the sample, so ^{1}HNMR spectroscopy was performed.

In the NMR spectrum presented below, it is possible to identify the following peaks:

- Assigned to the IL: δ = 8.8 (1H,s,3); δ = 7.4 (1H,s,5); δ = 7.3 (1H,s,6); δ = 4.2 (2H, t,J=6Hz,7); δ = 4 (3H, s,1); δ = 1.8 (2H, mult,8); δ = 1.3 (2H, mult,9); δ = 0.9 (3H, t,J=6Hz,10);
- Assigned to the $CDCl_3$: 7,26 (1H,s)
- Assigned to the H_2O: 1,52 (2H,s)
- Assigned to the acetone: 2.2 (s)

In the spectrum of figure 3.18 are still observed the following peaks:

δ =2.8 (s); δ =3.8 (s); δ =4.75 (s); δ =8.6 (s).

Again these peaks may be assigned acids formed by electrochemical reduction of CO_2 and to methanol, but without additional tests their presence cannot be confirmed.

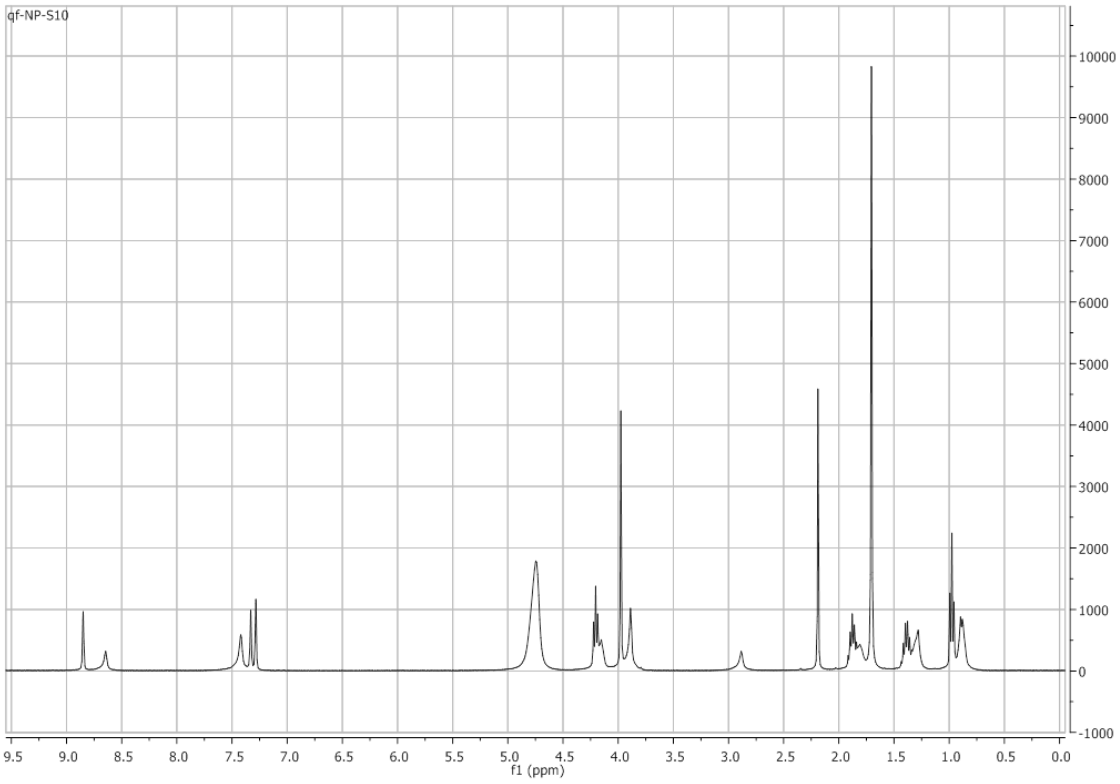


Figure 3.18 - Proton NMR spectrum of the electrolyte of the electrolysis carried out with an applied potential of -1.8V vs. Ag/Ag^{+}, at a temperature of 45ºC, at a pressure of 62.9 bar and 30 minutes reaction time (reaction 12).

3.1.4. Carbon electrode

3.1.4.1. Voltammetry

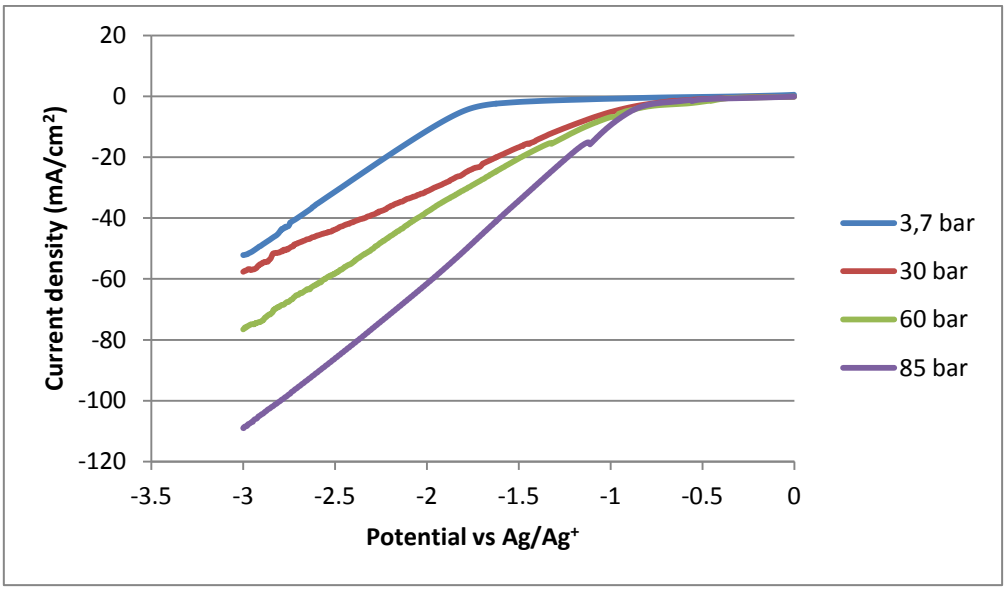


Figure 3.19 - Cathodic Curve 1st cycle with scan rate of 20 mV/s

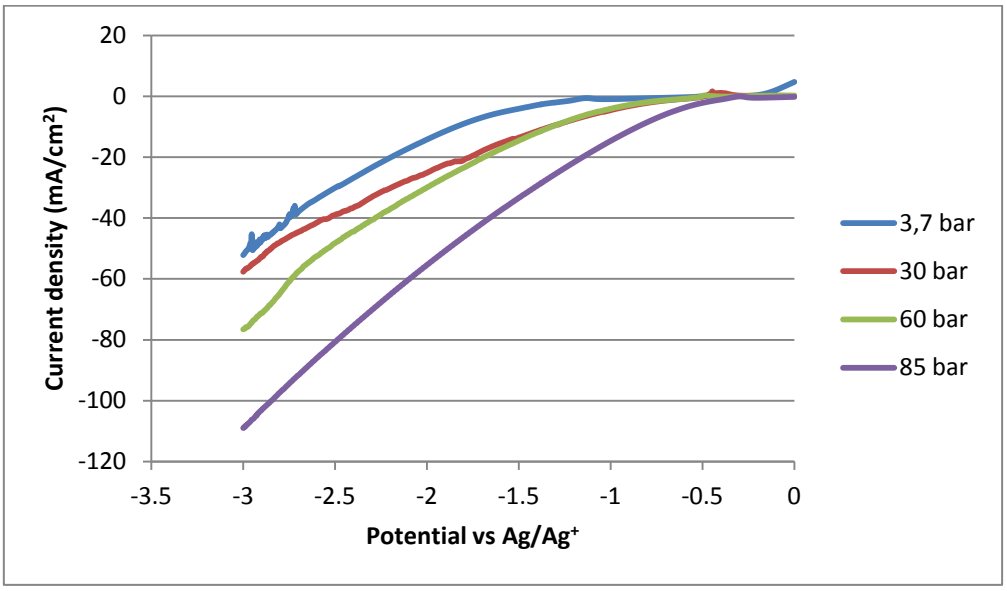


Figure 3.20 – Anodic Curve 1st cycle with scan rate of 20 mV/s

Figure 3.19 shows the cathodic curve at the carbon electrode in ionic liquid [bmim][BF_4] with 16-19% water as electrolyte, it was measured at 318 K and at different pressures. Argon was used as reference with a pressure of 3.4 bar, CO_2 was used for the other pressures. Observing figure 3.19 it turns out that the behavior of the carbon electrode is quite similar to Brass electrode, higher pressures yield higher currents. For all the pressures the onset potential for current increase was around -1 V vs. Ag/Ag^+.

Figure 3.20 shows the anodic curve of the same electrode in the same conditions, it is observed that there aren't oxidation waves for the pressure of 3.7 bar, 60 bar and 85 bar, but for pressure of 30 bar there is a small oxidation wave for a potential value of –0.5V vs. Ag/Ag^+.

3.1.4.2. Analysis of the gas phase

Electrolysis experiments were carried out using [bmim][BF_4] with 16-19% water as electrolyte as described in the experimental section 2.6. Electrolysis was performed potentiostatically and under stirring. The effect of carbon electrode in reduction of CO_2 using an applied potential of -1.8 V vs. Ag/Ag^+ at different pressures for the same electrolysis time and an applied potential of -2.4 V vs. Ag/Ag^+ at different pressures and different times of reaction was studied. The analysis of the gas phase was done by GC. The chromatograms can be observed in Annex 6.

Table 3.4 – Reactions conditions performed with carbon electrodes and GC results

Reaction	WE	CE	Applied Potential (V) vs. Ag/Ag^+	Conditions	Detection	Concentration (ppm)
13	C (2.3 cm^2)	Zn	-1.8	Pressure: 63.6 bar Temperature: 45ºC Time: 1 hour	CH_4 H_2	CH_4: Traces H_2: 462
14	C (1.8 cm^2)	Zn	-1.8	Pressure: 85.3 bar Temperature: 45ºC Time: 1 hour	H_2	H_2: 689
15	C (2.1 cm^2)	Zn	-2.4	Pressure: 62.5 bar Temperature: 45ºC Time: 1 hour	CH_4 H_2	CH_4: 1440 H_2: 3508
16	C (1.8 cm^2)	Zn	-2.4	Pressure: 84.7 bar Temperature: 45ºC Time: 3 hours	CH_4 H_2	CH_4: traces H_2: 1195

From the observation of table 3.4, it is possible to conclude that methane is formed on carbon electrode by CO2 reduction. Significant quantities were only produced at the more negative potential of -2.4 V vs Ag/A+. An increase in CO2 pressure does not seem to favor methane formation. More experiments must be carried out to confirm this trend.

3.1.4.3. Analysis of the liquid phase

The analysis of the liquid phase was done by ^{1}HNMR. In the NMR spectrum presented below, it is possible to identify the following peaks:

- Assigned to IL: δ = 8.8 (1H,s,3); δ = 7.4 (1H,s,5); δ = 7.3 (1H,s,6); δ = 4.2 (2H, t,J=6Hz,7); δ = 4 (3H, s,1); δ = 1.8 (2H, mult,8); δ = 1.3 (2H, mult,9); δ = 0.9 (3H, t,J=6Hz,10);
- Assigned to $CDCl_3$: 7,26 (1H,s)
- Assigned to H_2O: 1,52 (2H,s)
- Assigned to acetone: 2.2 (s)

In spectrum presented in figure 3.21 taken from the electrolyte after reaction 14 additional peaks are still observed:

δ = 4.7 – 5.2.

And in the figure 3.22:

δ = 4.8 – 5.5.

There are some broad bands in the Spectrum presented in figures 3.21 and 3.22, but again without performing additional tests it is not possible assign with certainty these peaks to a given compounds. A possibility to identify these peaks would be performing the NMR by adding a

compound we known in a sample of Ionic liquid plus water and check where the peak this peak appears, or if the intensity of existing peaks increase.

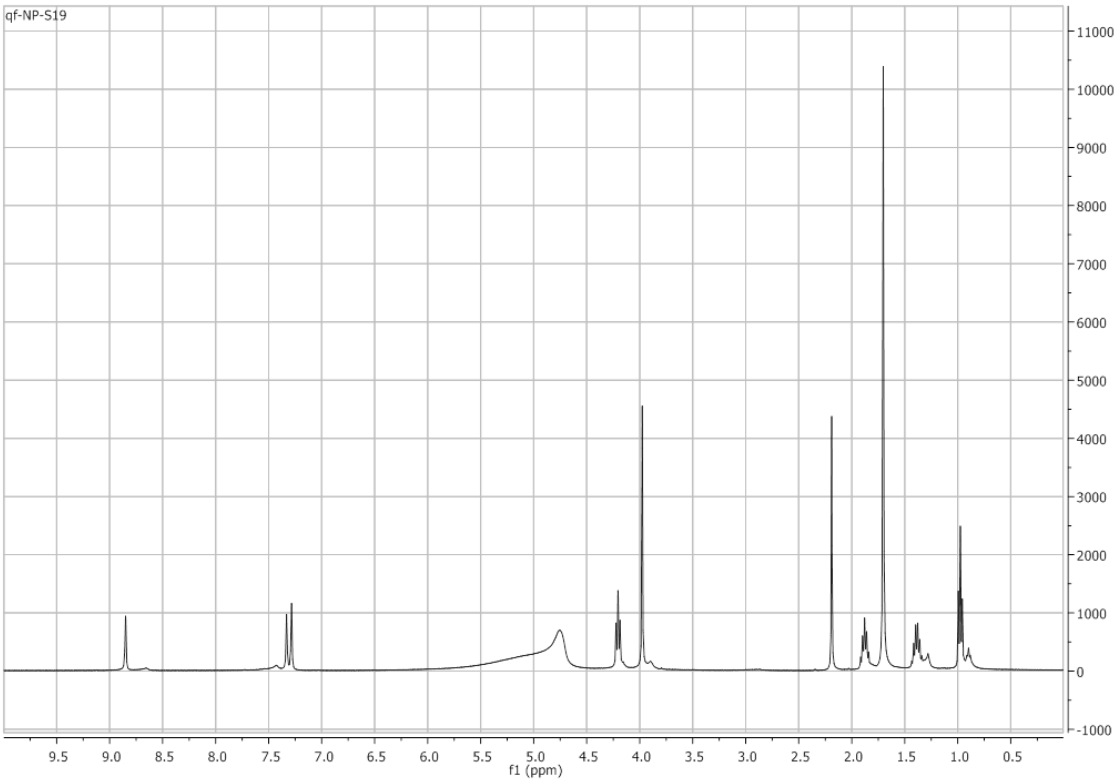


Figure 3.21 - Proton NMR spectrum of the electrolyte of the electrolysis carried out with an applied potential of -1.8V vs. Ag/Ag^{+}, at a temperature of 45ºC, at a pressure of 85.3 bar and 1 hour reaction time (reaction 14).

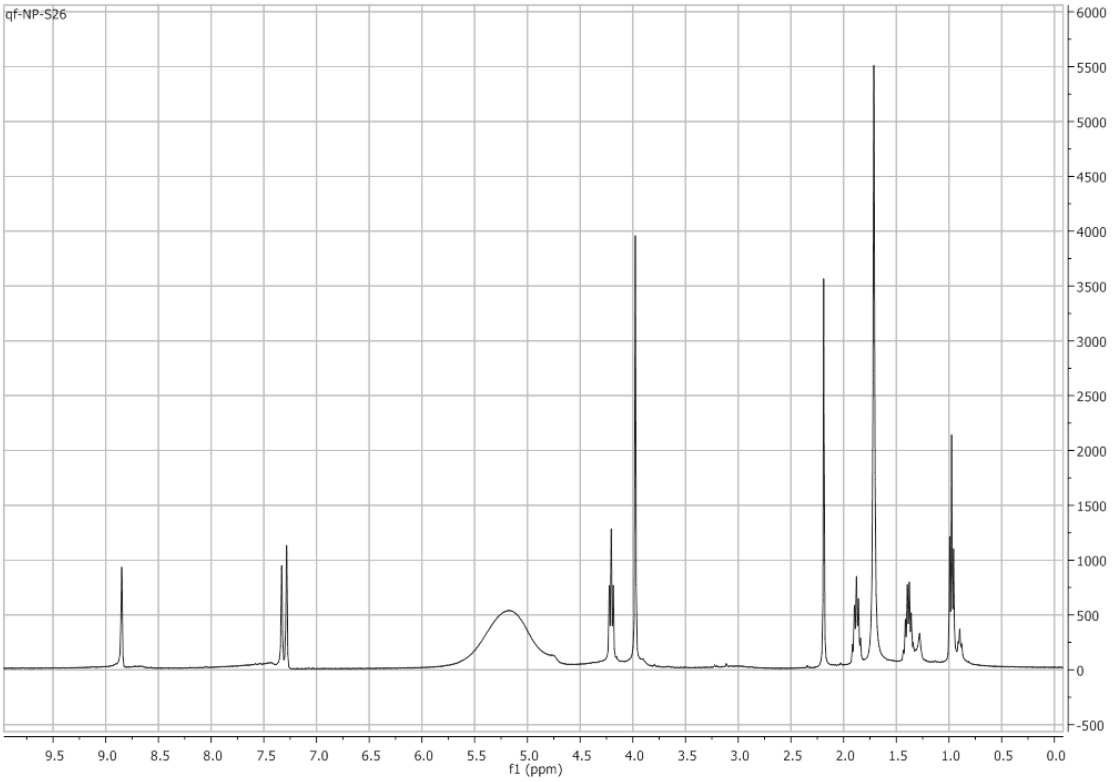


Figure 3.22 - Proton NMR spectrum of the electrolyte of the electrolysis carried out with an applied potential of -2.4V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 62.5 bar and 1 hour reaction time (reaction 15).

3.1.5. Electrodes coated with Nanoparticles of copper and nickel.

3.1.5.1. Analysis of the gas phase

Electrolysis experiments were carried out using [bmim][BF_4] with 16-19% water as electrolyte as described in the experimental section 2.6. Electrolysis was performed potentiostatically and under stirring. The analysis of the gas phase was done by GC. The chromatograms are presented in Annex 7.

Table 3.5 – Reactions performed with catalysts and GC results

Reaction	WE	CE	Applied Potential (V) vs. Ag/Ag^+	Conditions	Detection	Concentration (ppm)
17	OMN/NOVA/ NiCu-012 (1.8 cm^2)	Zn	-1.8	Pressure: 64.1 bar Temperature: 45ºC Time: 30 minutes	CH_4 H_2	CH_4: traces H_2: 1350
18	OMN/NOVA/ Ni-Cu013 (1.8 cm^2)	Zn	-1.8	Pressure: 62.5 bar Temperature: 45ºC Time: 1 hour	CH_4 H_2	CH_4: 1170 H_2: 12392
19	OMN/NOVA/ NiCu-Cu016 (1.4 cm^2)	Zn	-1.8	Pressure: 66.3 bar Temperature: 45ºC Time: 1 hour	H_2	CH_4: 1178 H_2: 22140

It is not possible to draw many conclusions from the results presented in table 3.5, since these were just initial tests to verify the behavior of catalytic materials and many more catalysts need to be prepared and tested.

3.1.5.2. Analysis of the liquid phase

Some samples of the liquid phase (electrolyte) were analysed by headspace-chromatography. In the chromatogram of the electrolyte after reactions 17 and 18, no peaks other than the blank can be observed. In the case of reaction 19 shown in figure 3.25, it is possible to observe a peak at 6.4 minutes and one peak in the beginning of the chromatogram assigned to a column impurity.

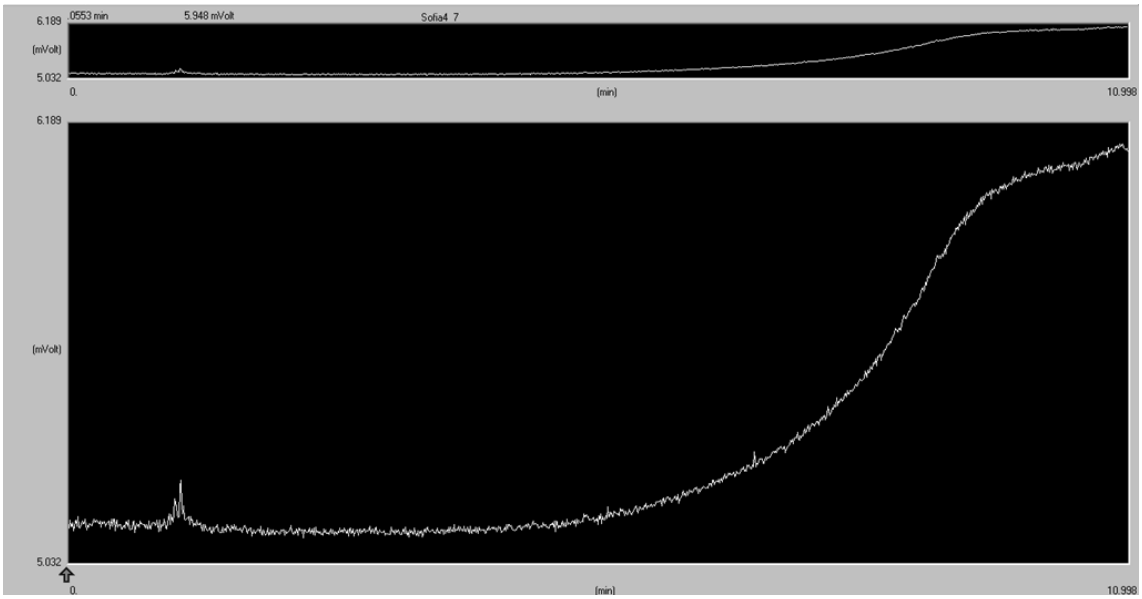


Figure 3.23 – Headspace gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 64.1 bar and 30 minutes reaction time (reaction 17).

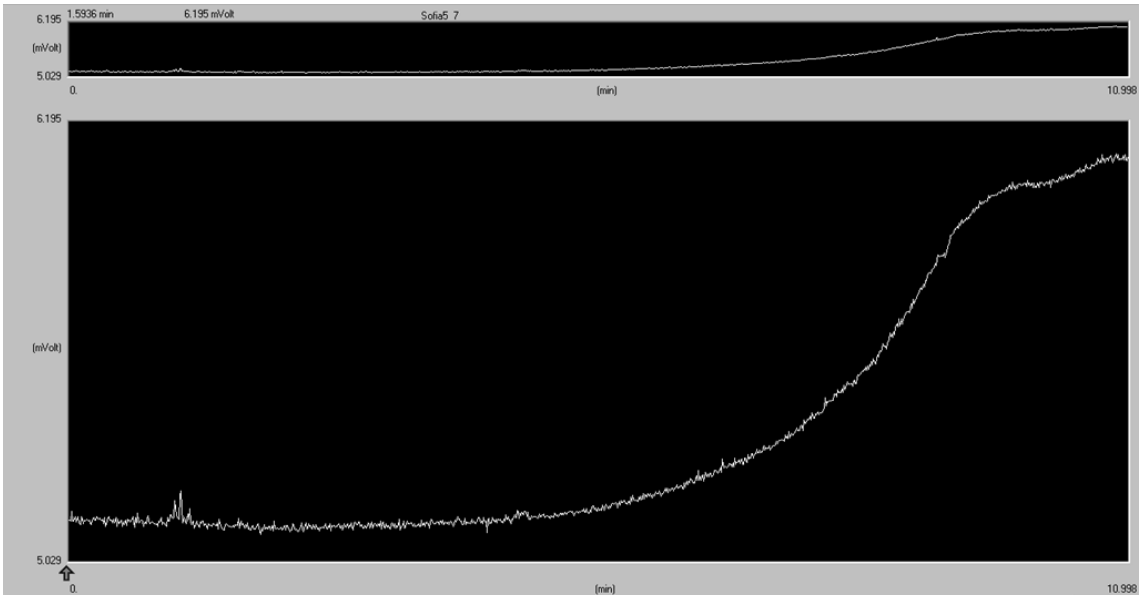


Figure 3.24 – Headspace gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 62.5 bar and 1 hour reaction time (reaction 18).

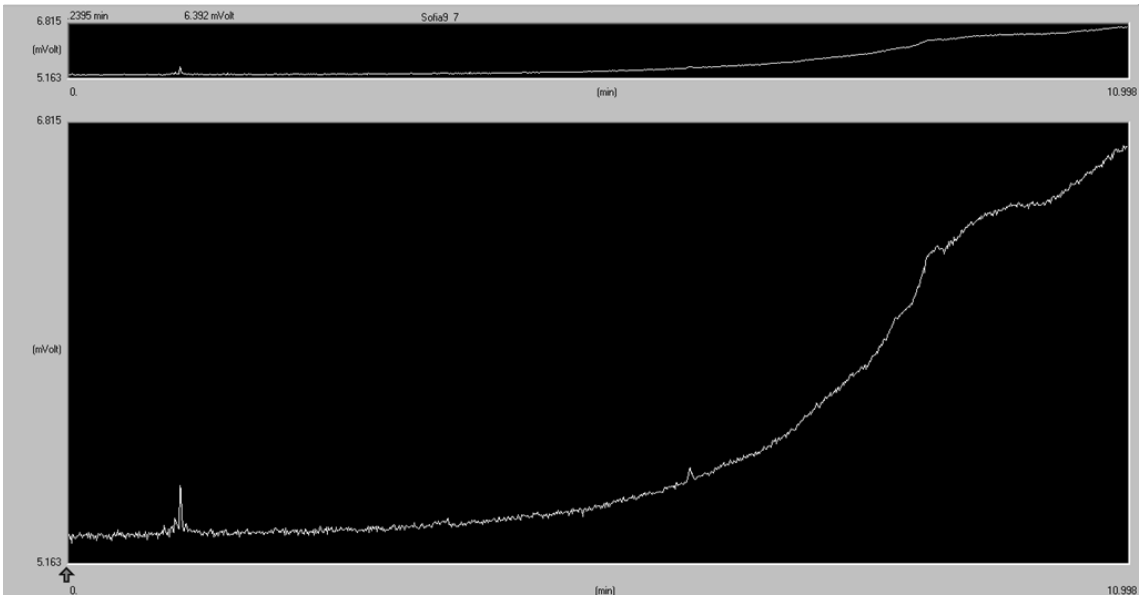


Figure 3.25 – Headspace gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 66.3 bar and 1 hour reaction time (reaction 19).

Again, the results do not allow us to conclude which are the compounds present in the sample, so it is necessary realized more additional tests. It has not possible to do de analysis by the ^{1}HNMR.

3.2. Electrodes comparison

Comparing the copper electrode with the brass electrode under the same electrolysis conditions, namely an applied potential applied at -1.8 V vs. Ag/Ag^{+}, at a pressure approximately of 60 bar and reaction time of 30 minutes the brass electrode performed better in terms of methane formation than the copper electrode.

Another interesting comparison that can be made is between the copper, carbon and nickel electrodes in electrolysis carried out in the following conditions: potential applied -1.8 V vs. Ag/Ag^{+}, pressure approximately of 85 bar and reaction time of 30 minutes for the copper electrode and 1 hour for nickel and carbon electrodes. The copper and nickel electrode have similar performance. It's an reasonable expectation that for 1 h electrolysis with the copper electrode would produce in these conditions more methane than the nickel electrode. Comparing copper, nickel and carbon electrodes performance in electrolysis at an applied potential of -1.8 V vs. Ag/Ag^{+}, at a pressure approximately of 60 bar and reaction time of 1 hour the nickel electrode seems to be better.

Comparing the nickel electrode and the carbon electrode, same conditions namely: potential applied at -2.4 V, pressure approximately 85 bar and reaction time of 3 hour. It was found that the best result under these conditions for the electrochemical reduction of CO2 to methane is obtained when the nickel electrode was used.

Analyzing all the results presented earlier for each electrode, it should be noted that the electrode which yielded the best production of methane was the brass electrode. This result was obtained with a potential at -2.4 V vs. Ag/Ag^{+} and with a reaction time of 2 hours. Considering the good performance of the copper foam electrode and as one objective of this research program is to develop an energetically efficient electrode (working at less negative potentials) and with high activity for methane production, a copper foam electrode with a zinc deposit would be a good candidate for testing.

4. Conclusion

This work, studied the electrochemical reduction of CO_2 using an ionic liquid as an electrolyte. To this end, several experiments were carried out using the Ionic liquid BMIMBF4 with 16-19% of water as electrolyte and several working electrodes were tested.

The conclusions obtained from this work were first acquired from the study of the cyclic voltammetry for the different electrodes. In the case of the copper working electrode it has been established that the highest currents are obtained for the electrolysis carried out at 60 bar. The current starts to increase at a potential of -1.3 V vs. Ag/Ag^+. From the Ni electrode it can be concluded that the currents is practically the same for all pressures studied and the onset potential was around -1.2 V vs. Ag/Ag^+, but an increase of the current from the potential -2.4 V vs. Ag/Ag^+ was observed. In what concerns the brass electrode the onset potential is around -1.2 V vs. Ag/Ag^+ and it can be concluded that current increase with increasing CO_2 pressure. The carbon electrode has the onset potential around -1 V vs. Ag/Ag^+, and we observed that the higher pressures yield higher currents.

Analyzing the reactions using the copper electrode, it can be concluded that methane starts to be produced significantly at voltages higher than -1.3 V vs. Ag/Ag+ at 60 bar pressure. The best result for methane conversion in the conditions studied was obtained when a Cu foam was used. In the case of nickel electrode the largest methane production was obtained with the following working conditions: pressure at 60 bar, potential at -1.8 V vs. Ag/Ag^+ and a reaction time of 1 hour. For the brass electrode, more tests must be carried out to be able to draw any conclusion. In the case of the carbon electrode we can conclude that the best conditions for the production of methane was with the lower pressure of 60 bar and the more negative potential of -2.4 V vs. Ag/Ag^+.

Regarding the reactions carried out with the working electrodes studied, it can be concluded that the electrode with better results for production of methane was the brass electrode with a potential at -2.4 V vs. Ag/Ag^+ and a reaction time of 2 hours. However, one objective of this research program is to develop an energetically efficient electrode (working at less negative potentials) and with high activity for methane production. So, considering the good performance of the copper foam, will be interesting to do a test with the copper foam electrode with a zinc deposit.

From the results of the analysis of the liquid phases, after the reactions, it was possible to conclude that in most of the reactions there was production of some components, unfortunately it has not been possible to find out what are these components, so it would be necessary to conduct further tests, such as analyzing the liquid phase by mass spectroscopy or even by analyzing by NMR a sample of the ionic liquid plus water with the addition a known compound check where the peak appears, or if the intensity of existing peaks increase.

5. References

[1] B. Hu, C. Guild and S. Suib, "Thermal, electrochemical, and photochemical conversion of CO2 to fuels and value-added products," *Journal of CO2 Utilization,* pp. 18-27, 2013.

[2] J. Yano, T. Morita , K. Shimano , Y. Nagani and S. Yamasaki, "Selective ethylene formation by pulse-mode electrochemical reduction of carbon dioxide using copper and copper-oxide electrodes," *Solid State Electrochem,* pp. 554-557, 2007.

[3] J. Lee, Y. Kwon, R. Machunda and H. J. Lee, "Electrocatalytic Recycling of CO2 and Small organic Molecules," *Chem. Asian J.,* pp. 1516-1523, 2009.

[4] B. Metz, O. Davidson, H. Coninck, M. Loos and L. Meyer, Carbon Dioxide Capture and Storage, Cambridge University Press, 2005.

[5] *European Cement Research Academy,,* Technical Report TR-ECRA-106/2009.

[6] Q. Feng, S. Liu, X. Wang and G. Jin, "Nanoporous copper incorporated platinum composites for electrocatalytic reduction of CO2 in ionic liquid BMIMBF4," *Applied Surface Science,* vol. 258, pp. 5005-5009, 2012.

[7] G. Zhao, T. Jiang, B. Han, Z. Li, J. Zhang, Z. Liu, J. He and W. Wu, "Electrochemical reduction of supercritical carbon dioxide in ionic liquid 1-n-butyl-3-methylimidazolum hexafluorophosphate," *The Journal of Supercritical Fluids,* pp. 287-291, 2004.

[8] S. Kaneco, H. Katsumata , T. Suzuki and K. Ohta, "Electrochemical reduction of CO2 to Methane at the Cu electrode in methanol with sodium supporting salts and Comparison with other alkaline salts," *Energy & Fuels,* pp. 409-414, 2006.

[9] M. Gattrell, N. Gupta and A. Co, "Electrochemical reduction of CO2 to hydrocarbons to store renewable electrical energy and upgrade biogas," *Energy Conversion & Management,* pp. 1255-1265, 2007.

[10] A. O'Mahony, D. Silvester, L. Aldous, C. Hardacre and R. Compton, "Effect of water on the electrochemical window and potential limits of room-temperarute ionic liquid," *J. Chem. Eng.,* pp. 2884-2891, 2008.

[11] Z. Zhang, Y. Xie, W. Li, S. Hu, J. Song, T. Jiang and B. Han, "Hydrogenation of carbon dioxide is promoted by a task-specific ionic liquid," *Angewandte Chemie,* pp. 1143-1145, 2008.

[12] H. Yang, Y. Gu, Y. Deng and F. Shi, "Electrochemical activation of carbon dioxide in ionic liquid: synthesis of cyclic carbonates at mild reaction conditions," *Chem. Coommun.,* pp. 274-275, 2002.

[13] M. Althuluth, M. Mota-Martinez, M. Kroon and C. Peters, "Solubility of Carbon Dioxide in the Ionic Liquid 1-Ethyl-3-methylimidazoluim Tris(pentafluoroethyl)trifluorophosphate," *Journal of Chemival & Engineering,* pp. 3422-3425, 2012.

[14] D. K. Gosser Jr., Cyclic Voltammetry, Wiley-VCH, 2005.

[15] J. Wang, Analytical Electrochemistry, Wiley-VCH, 2000.

[16] U. Schroder, J. Wadhawan, R. Compton, F. Marken, P. suarez, C. Consorti, R. Souza and J. Dupont, "Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(S)-dimethylocten-2-yl]imidazolium tetrafluoroborate, 1-butyl-3-methylimidazoliumtetrafluoroborate and hexafluorophosphate ionic liquids.," *New J. Chem.,* pp. 1009-1015, 2000.

[17] L. E. Barrosse-Antle, A. Bond, R. Compton, A. O'Mahony, E. Rogers and D. Silvester, "Voltammetry in Room Temperature Ionic Liquid: Comparisons and Contrasts with Conventional Electrochemical solvents," *Chem. Asian J.,* pp. 202-230, 2010.

[18] R. Chang, General Chemistry, 2003.

[19] R. Jain, Physics, 2006.

[20] K. Hara, A. Tsuneto, A. Kudo and T. Sakata, "Electrochemical reduction of CO2 on a Cu electrode under High Pressure," *J. electrochemical Society,* vol. 141, pp. 2097-2103, 1994.

[21] Y. Hori, A. Murata and R. Takahashi, "Formation of hydrocarbons in the electrochemical reduction of carbon dioxide at a copper electrode in aqueous solution," *J. Chem. Soc.,* pp. 2309-2326, 1989.

[22] K. Hara, A. Kudo and T. Sakata, "Electrochemical reduction of carbon dioxide under high pressure on various electrode in an aqueous electrolyte," *Journal of Electroanalytical Chemistry,* pp. 141-147, 1995.

[23] T. Saeki, K. Hashimoto, N. Kimura, K. Omata and A. Fujishima, "Electrochemical reduction of CO2 with high current density in a CO2 + methanol medium at various metal electrodes," *Journal of Electroanalytical Chemistry ,* pp. 299-302, 1996.

[24] S. Kaneco, K. Liba, H. Katsumata, T. Suzuki and K. Ohta, "Electrochemical reduction of high pressure CO2 at a Cu electrode in cold methanol," *Electrochimica Acta,* pp. 4880-4885, 2006.

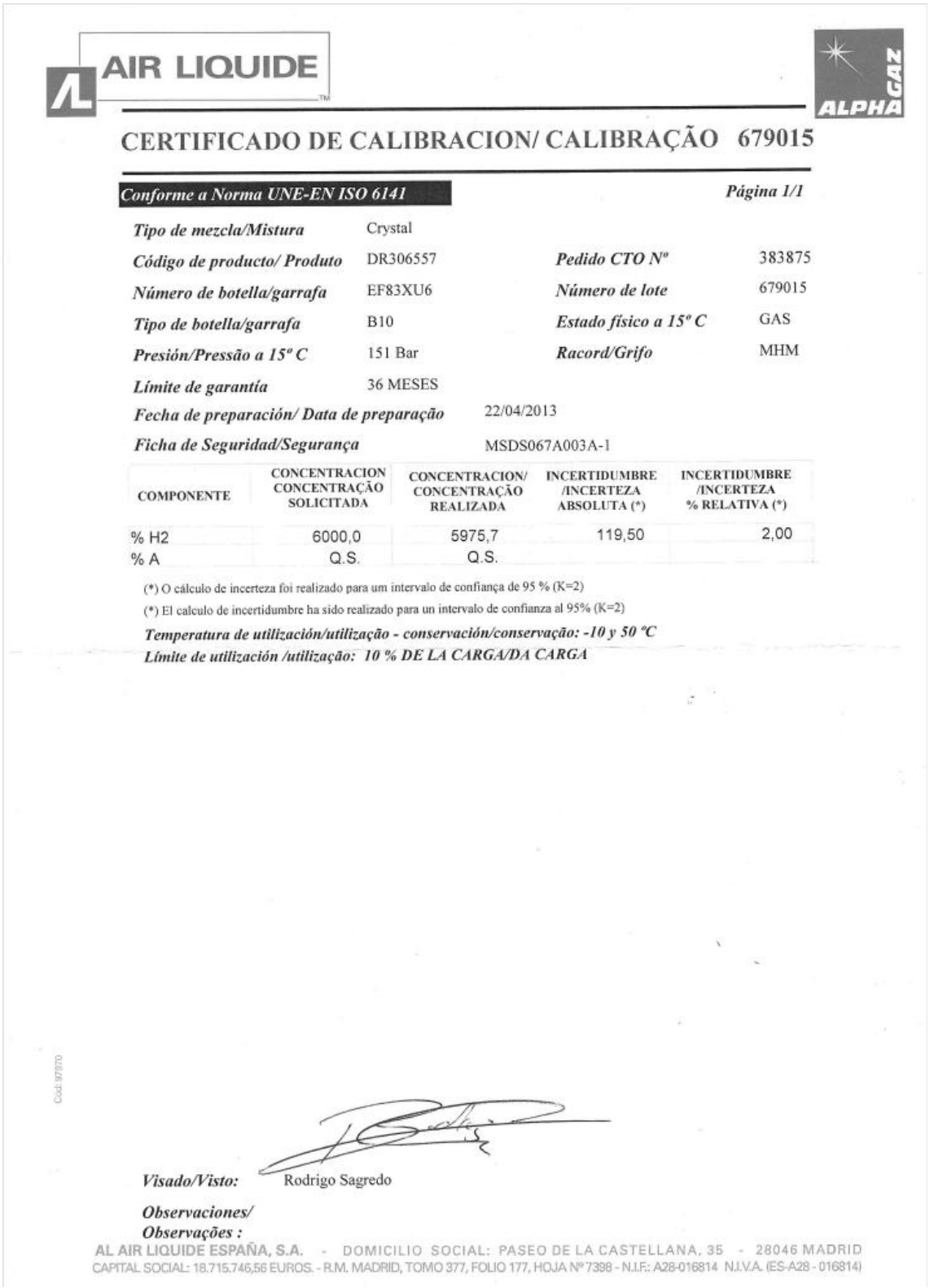
[25] L. Barrosse-Antle and R. Compton, "Reduction of carbon dioxide in 1-butyl-3-methylimidazolium acetate," *The Royal Society of Chemistry,* pp. 3744-3746, 2009.

[26] L. Snuffin, L. Whaley and L. Yu, "Catalytic electrochemical reduction of CO2 ionic liquid EMIMBF3Cl," *Journal of the electrochemical Society,* pp. 155-158, 2011.

[27] G. Fulmer, A. Miller, N. Sherden, H. Gottlieb, A. Nudelman, B. Stoltz, J. Bercaw and K. Goldberg, *NMR chemical shifts of traces impurities: common laboratory solvents, organics, and gases in deuterated solvents relevant to organometallic chemist,* 2010, pp. 2176-2179.

6. Annex

Annex 1 – Calibration Certificate of Hydrogen



AIR LIQUIDE

ALPHA GAZ

CERTIFICADO DE CALIBRACION/ CALIBRAÇÃO 679015

Conforme a Norma UNE-EN ISO 6141 *Página 1/1*

Tipo de mezcla/Mistura	Crystal		
Código de producto/ Produto	DR306557	*Pedido CTO Nº*	383875
Número de botella/garrafa	EF83XU6	*Número de lote*	679015
Tipo de botella/garrafa	B10	*Estado físico a 15º C*	GAS
Presión/Pressão a 15º C	151 Bar	*Racord/Grifo*	MHM
Límite de garantía	36 MESES		
Fecha de preparación/ Data de preparação	22/04/2013		
Ficha de Seguridad/Segurança	MSDS067A003A-1		

COMPONENTE	CONCENTRACION CONCENTRAÇÃO SOLICITADA	CONCENTRACION/ CONCENTRAÇÃO REALIZADA	INCERTIDUMBRE /INCERTEZA ABSOLUTA (*)	INCERTIDUMBRE /INCERTEZA % RELATIVA (*)
% H2	6000,0	5975,7	119,50	2,00
% A	Q.S.	Q.S.		

(*) O cálculo de incerteza foi realizado para um intervalo de confiança de 95 % (K=2)

(*) El calculo de incertidumbre ha sido realizado para un intervalo de confianza al 95% (K=2)

Temperatura de utilización/utilização - conservación/conservação: -10 y 50 ºC

Límite de utilización /utilização: 10 % DE LA CARGA/DA CARGA

Cod: 97970

Visado/Visto: Rodrigo Sagredo

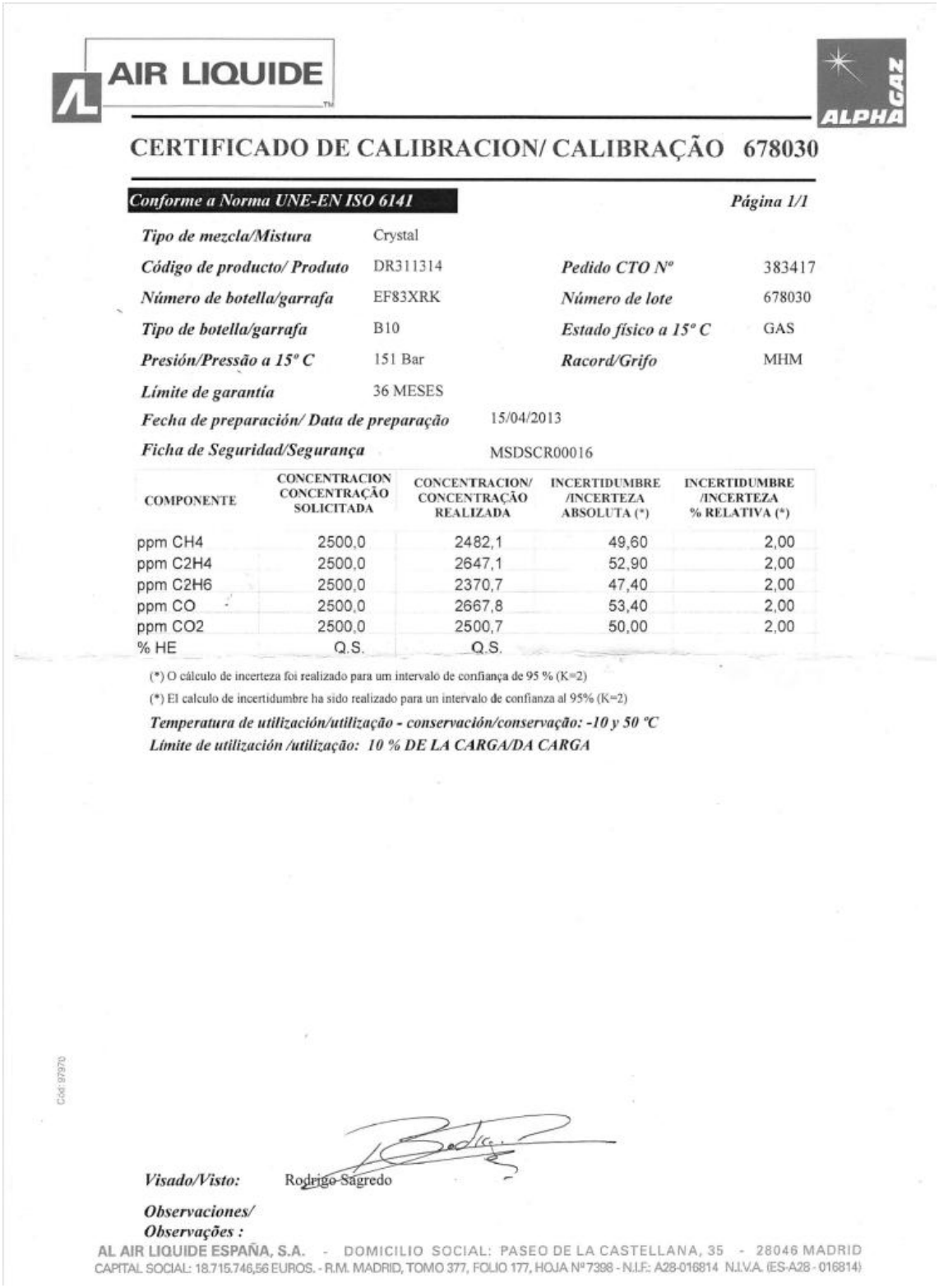
Observaciones/ Observações :

AL AIR LIQUIDE ESPAÑA, S.A. - DOMICILIO SOCIAL: PASEO DE LA CASTELLANA, 35 - 28046 MADRID

CAPITAL SOCIAL: 18.715.746,56 EUROS. - R.M. MADRID, TOMO 377, FOLIO 177, HOJA Nº 7398 - N.I.F.: A28-016814 N.I.V.A. (ES-A28 - 016814)

Figure 6.1 – Calibration Certificate of hydrogen

Annex 2 – Calibration certificate for hydrocarbons



AIR LIQUIDE

ALPHA GAZ

CERTIFICADO DE CALIBRACION/ CALIBRAÇÃO 678030

Conforme a Norma UNE-EN ISO 6141 — *Página 1/1*

Tipo de mezcla/Mistura	Crystal		
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Número de botella/garrafa	EF83XRK	*Número de lote*	678030
Tipo de botella/garrafa	B10	*Estado físico a 15º C*	GAS
Presión/Pressão a 15º C	151 Bar	*Racord/Grifo*	MHM
Límite de garantía	36 MESES		

Fecha de preparación/ Data de preparação 15/04/2013

Ficha de Seguridad/Segurança MSDSCR00016

COMPONENTE	CONCENTRACION CONCENTRAÇÃO SOLICITADA	CONCENTRACION/ CONCENTRAÇÃO REALIZADA	INCERTIDUMBRE /INCERTEZA ABSOLUTA (*)	INCERTIDUMBRE /INCERTEZA % RELATIVA (*)
ppm CH4	2500,0	2482,1	49,60	2,00
ppm C2H4	2500,0	2647,1	52,90	2,00
ppm C2H6	2500,0	2370,7	47,40	2,00
ppm CO	2500,0	2667,8	53,40	2,00
ppm CO2	2500,0	2500,7	50,00	2,00
% HE	Q.S.	Q.S.		

(*) O cálculo de incerteza foi realizado para um intervalo de confiança de 95 % (K=2)

(*) El calculo de incertidumbre ha sido realizado para un intervalo de confianza al 95% (K=2)

Temperatura de utilización/utilização - conservación/conservação: -10 y 50 ºC

Límite de utilización /utilização: 10 % DE LA CARGA/DA CARGA

Cód: 97970

Visado/Visto: Rodrigo Sagredo

Observaciones/ Observações :

AL AIR LIQUIDE ESPAÑA, S.A. - DOMICILIO SOCIAL: PASEO DE LA CASTELLANA, 35 - 28046 MADRID

CAPITAL SOCIAL: 18.715.746,56 EUROS. - R.M. MADRID, TOMO 377, FOLIO 177, HOJA Nº 7398 - N.I.F.: A28-016814 N.I.V.A. (ES-A28 - 016814)

Figure 6.2 – Calibration certificate for hydrocarbons

Annex 3 – Chromatograms of the reactions with the copper electrode

Reaction 1

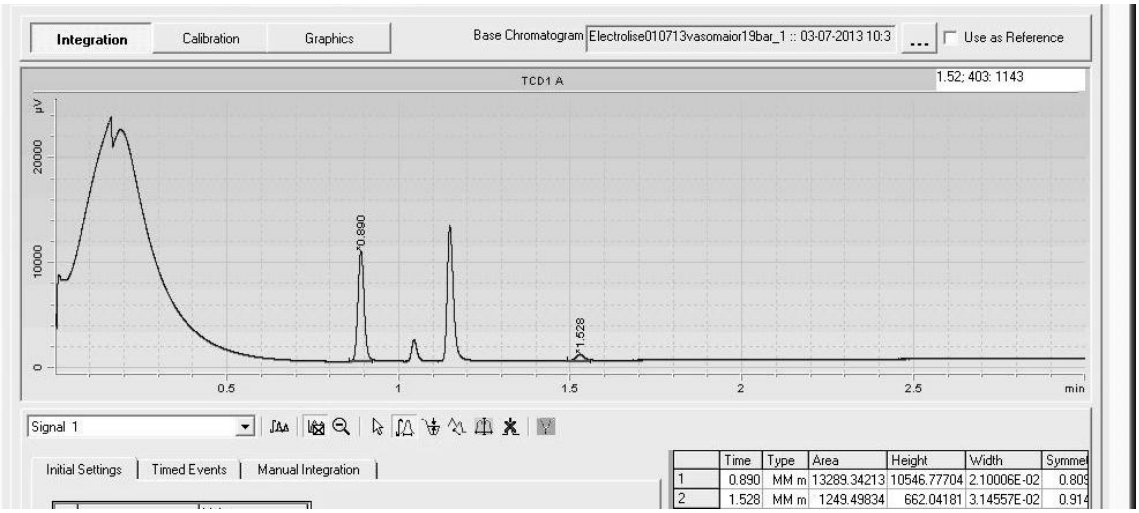

Figure 6.3 – Channel 1 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 60 bar and 1 hour reaction time (reaction 1)

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.890 min) and methane (tr = 1.528 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

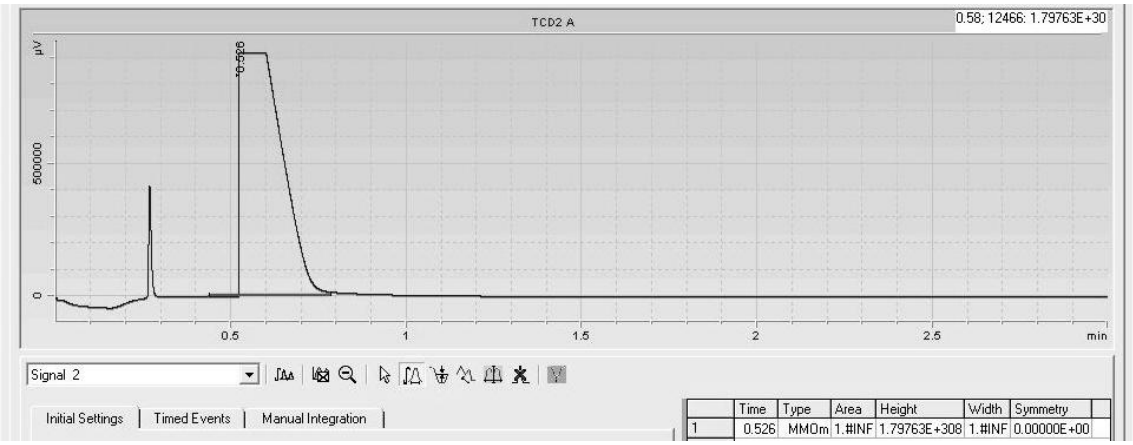

Figure 6.4 – Channel 2 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 60 bar and 1 hour reaction time (reaction 1)

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.526 min)

Reaction 2

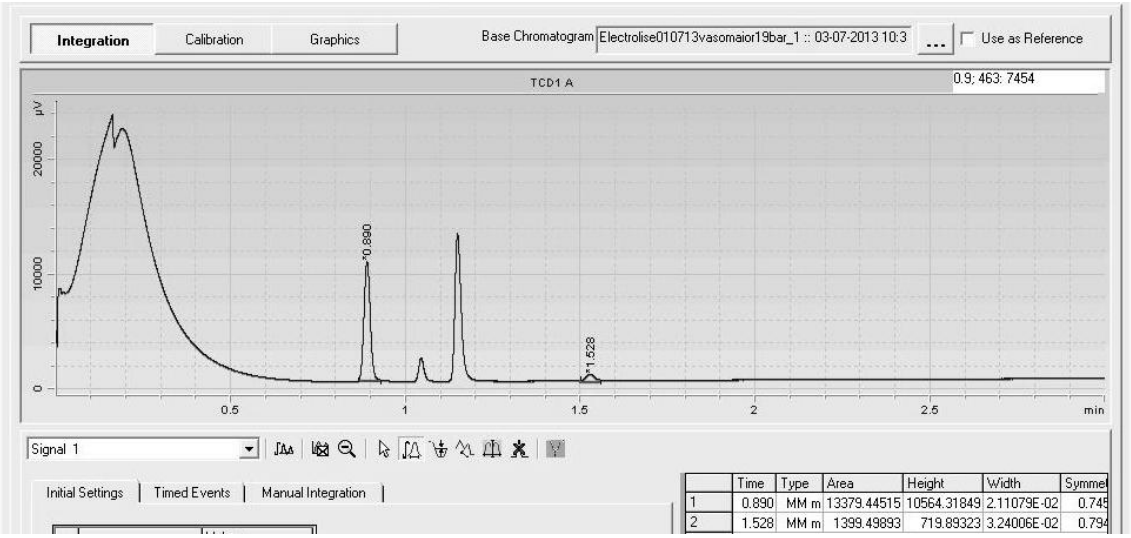

Figure 6.5 – Channel 1 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 66.5 bar and 30 minutes reaction time (reaction 2)

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.890 min) and methane (tr = 1.528 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

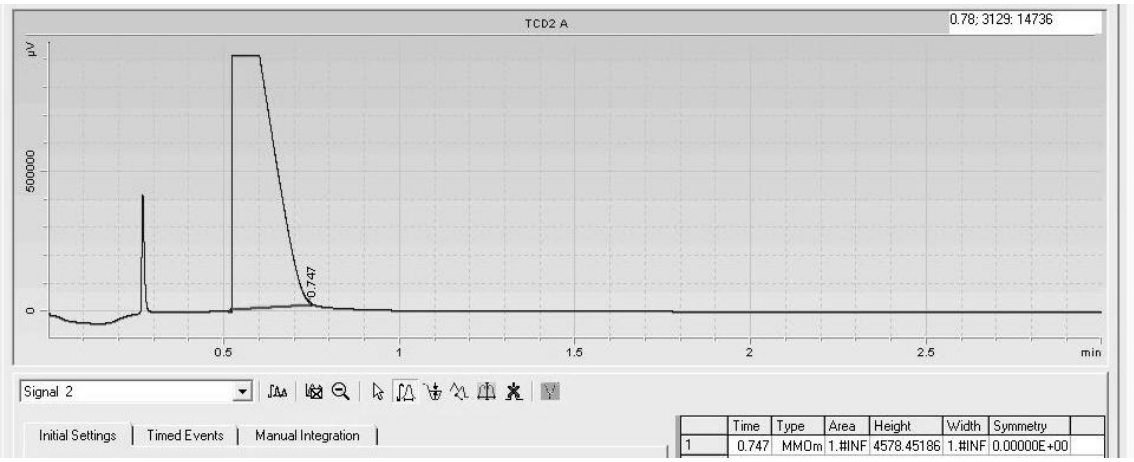

Figure 6.6 – Channel 2 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 66.5 bar and 30 minutes reaction time (reaction 2)

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.7 min)

Reaction 3

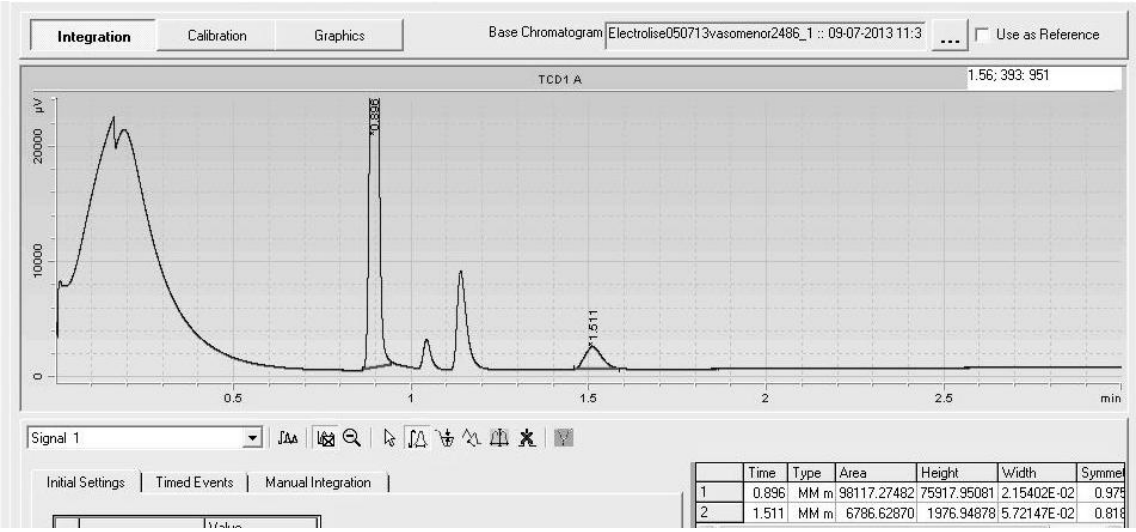

Figure 6.7 – Channel 1 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 64.5 bar and 13 minutes reaction time (reaction 3)

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.896 min) and methane (tr = 1.511 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

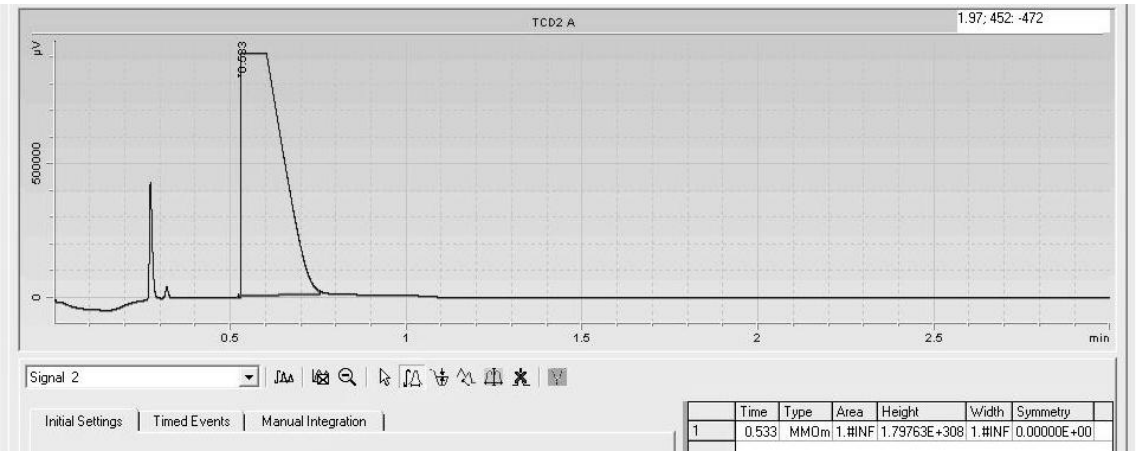

Figure 6.8 – Channel 2 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 64.5 bar and 13 minutes reaction time (reaction 3)

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.533 min)

Reaction 4

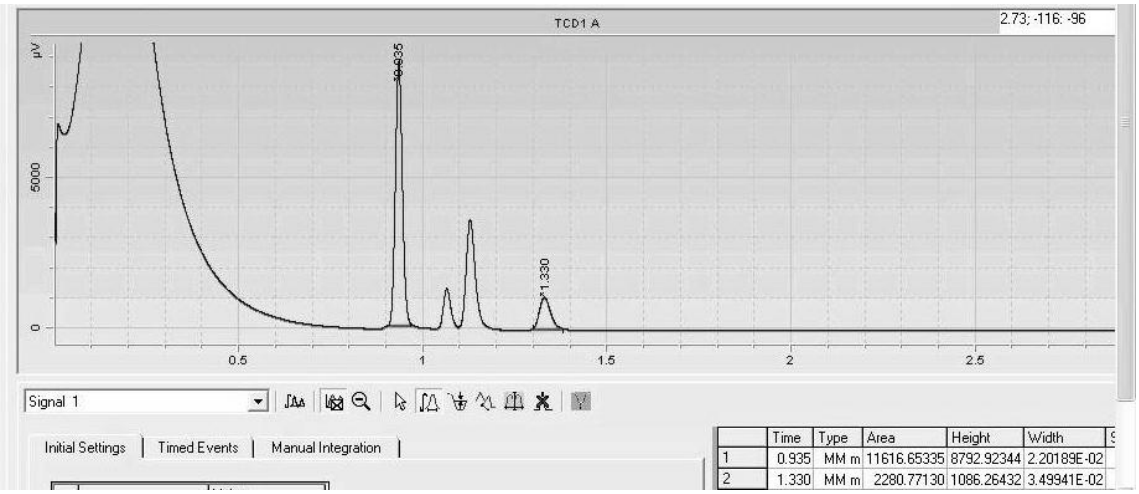

Figure 6.9 – Channel 1 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85 bar and 30 minutes reaction time (reaction 4).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.935 min) and methane (tr = 1.330 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

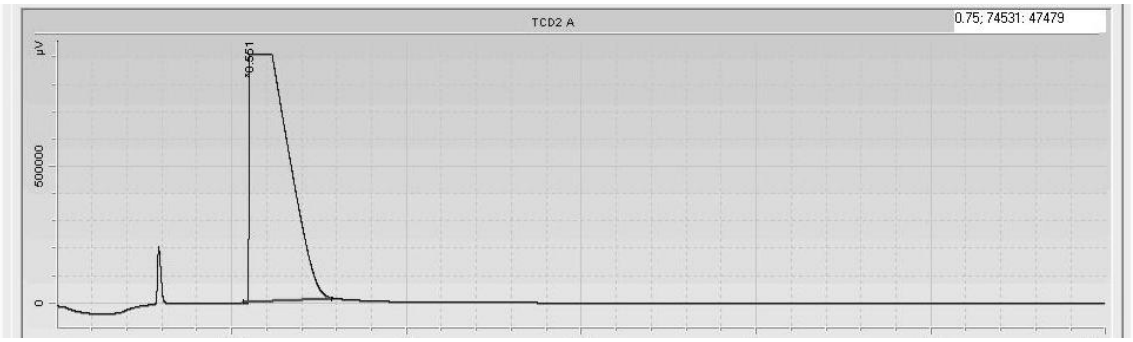

Figure 6.10 – Channel 2 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85 bar and 30 minutes reaction time (reaction 4).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.561 min)

Reaction 5

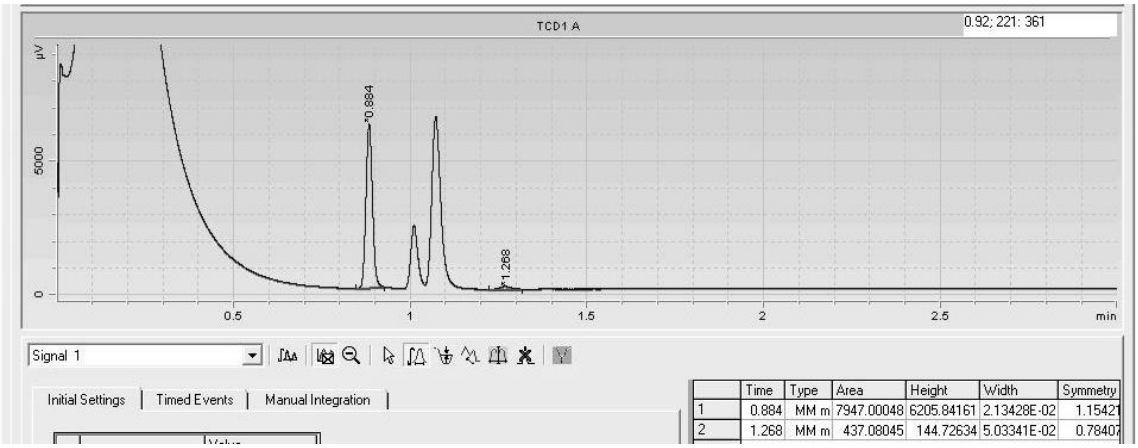

Figure 6.11 – Channel 1 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.3 V vs. Ag/Ag$^+$, at a temperature of 45ºC, at a pressure of 66.3 bar and 30 minutes reaction time (reaction 5).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.884 min) and methane (tr = 1.268 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

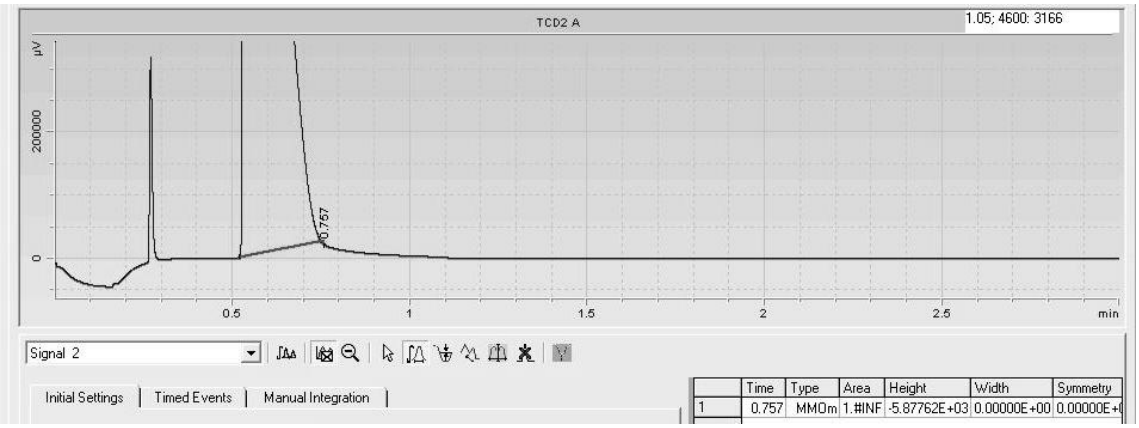

Figure 6.12 - Channel 2 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.3 V vs. Ag/Ag$^+$, at a temperature of 45ºC, at a pressure of 66.3 bar and 30 minutes reaction time (reaction 5).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.757 min)

Reaction 6

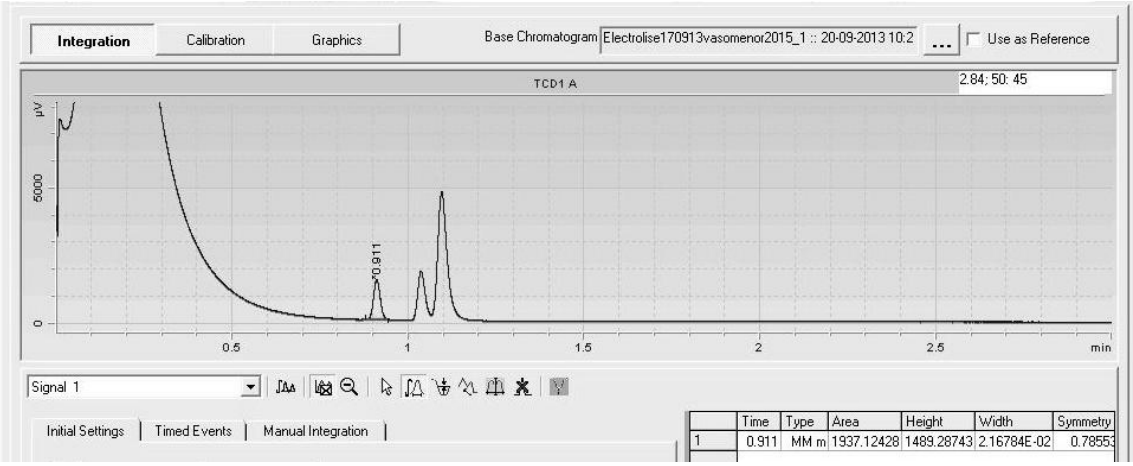

Figure 6.13 – Channel 1 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -0.5 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 63.1 bar and 30 minutes reaction time (reaction 6)

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.911 min) methane was not detected. Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

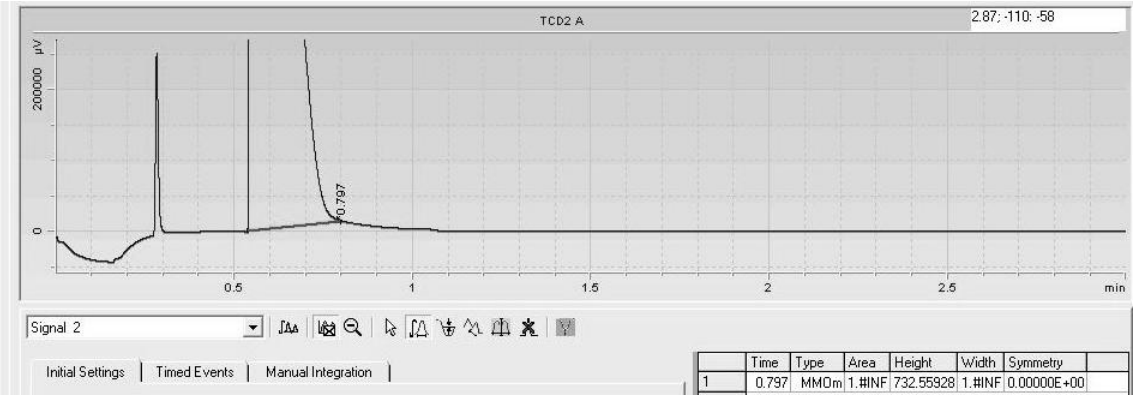

Figure 6.14 – Channel 2 of the Gas chromatogram of CO_2 electrolysis carried out with an applied potential at -0.5 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 63.1 bar and 30 minutes reaction time (reaction 6)

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.797 min)

Annex 4 – Chromatograms of the reactions with the nickel electrode

Reaction 7

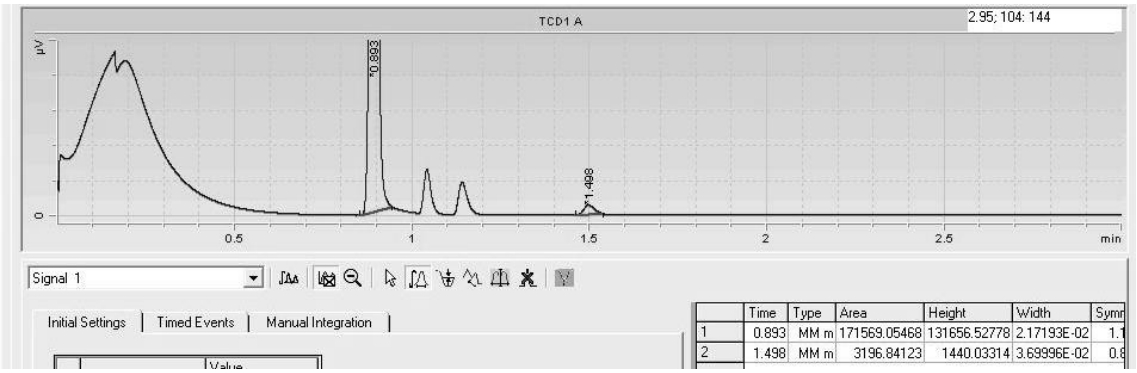

Figure 6.15 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -2.4 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 86 bar and 3 hours reaction time (reaction 7).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.893 min) and methane (tr = 1.498 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

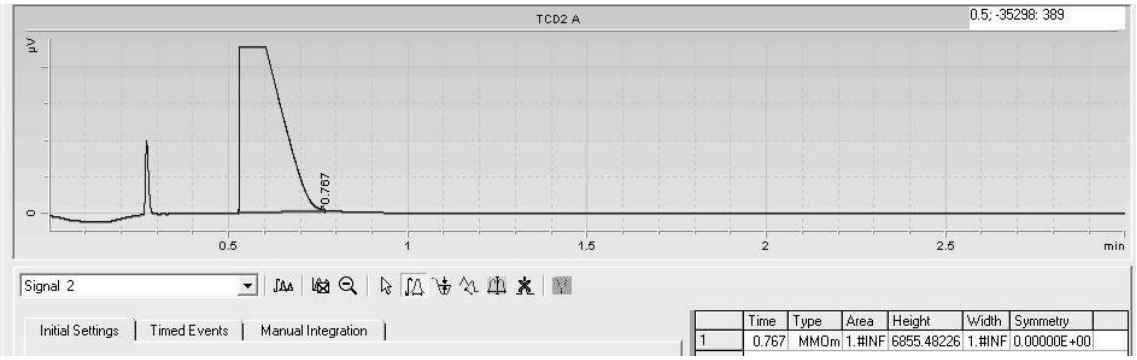

Figure 6.16 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -2.4 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 86 bar and 3 hours reaction time (reaction 7).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.767 min)

Reaction 8

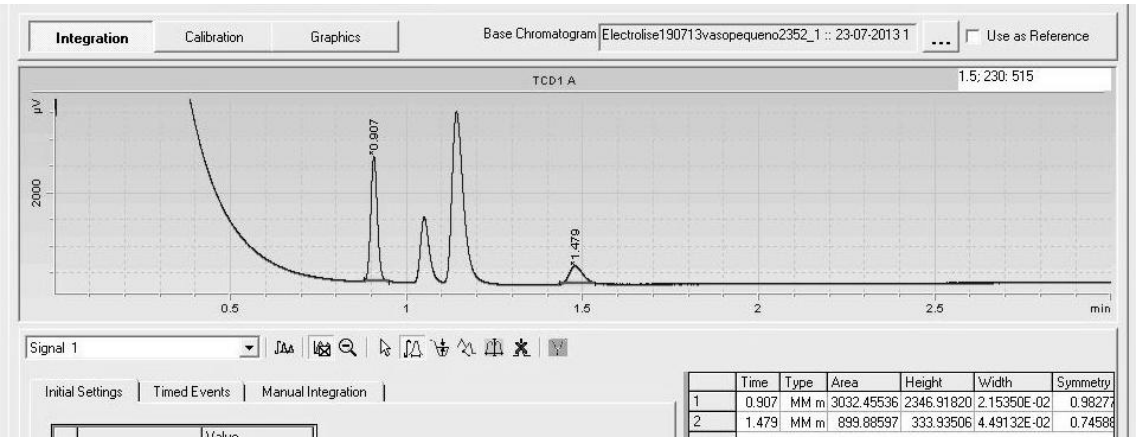

Figure 6.17 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85.5 bar and 1 hour reaction time (reaction 8).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.907 min) and methane (tr = 1.479 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

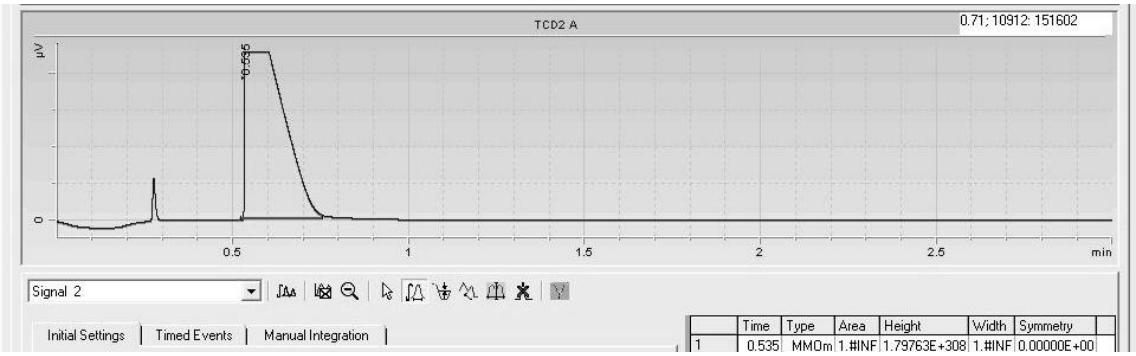

Figure 6.18 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85.5 bar and 1 hour reaction time (reaction 8).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.535 min)

Reaction 9

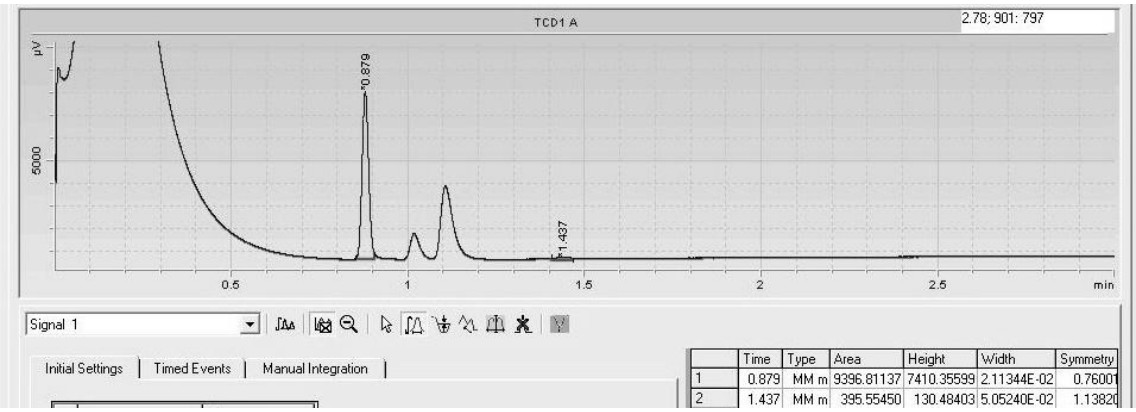

Figure 6.19 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.6 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85.3 bar and 1 hour reaction time (reaction 9).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.879 min) and methane (tr = 1.437 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

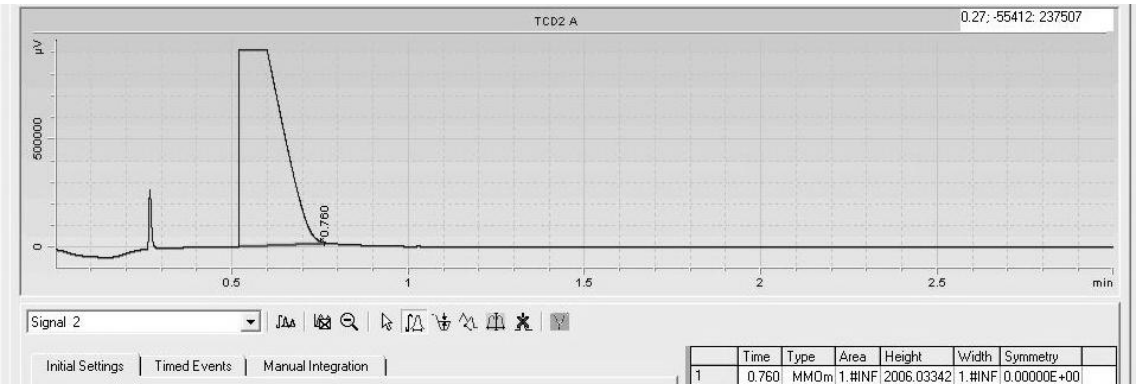

Figure 6.20 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.6 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85.3 bar and 1 hour reaction time (reaction 9).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.760 min)

Reaction 10

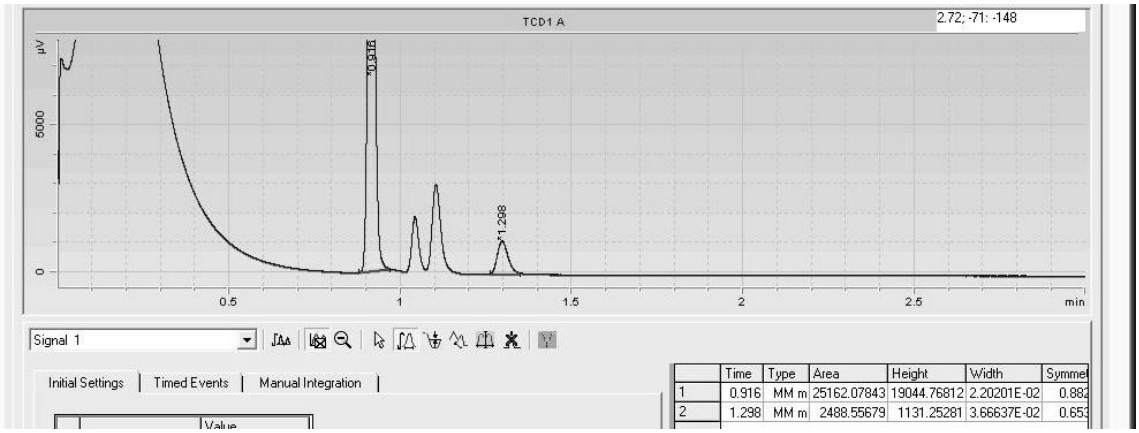

Figure 6.21 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 61.1 bar and 1 hour reaction time (reaction 10).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.916 min) and methane (tr = 1.298 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

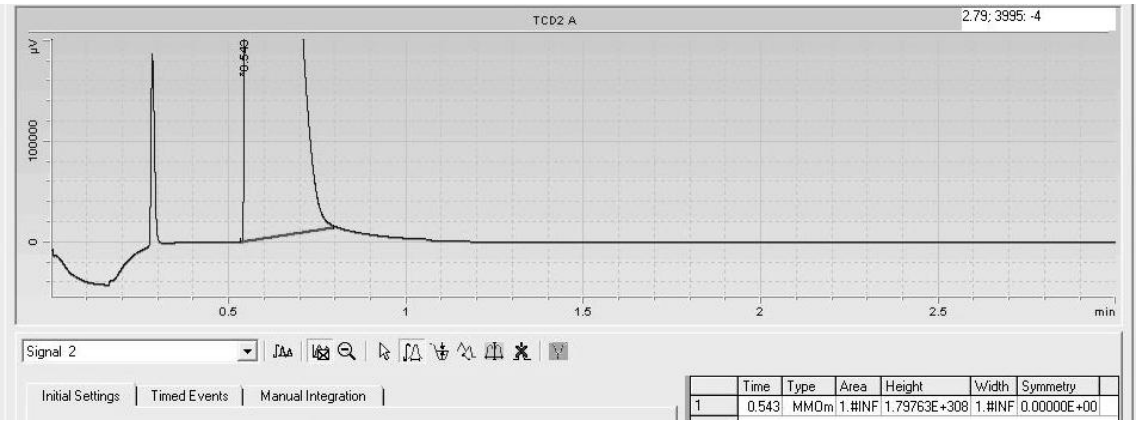

Figure 6.22 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 61.1 bar and 1 hour reaction time (reaction 10).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.543 min)

Annex 5 – Chromatograms of the reactions with the brass electrode

Reaction 11

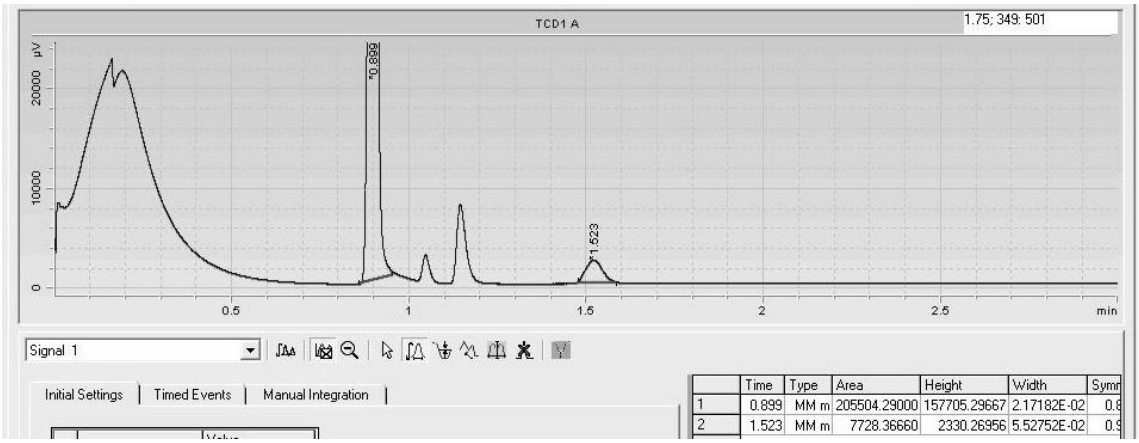

Figure 6.23 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -2.4 V vs. Ag/Ag$^+$, at a temperature of 45ºC, at a pressure of 63.3 bar and 2 hours reaction time (reaction 11).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.899 min) and methane (tr = 1.523 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

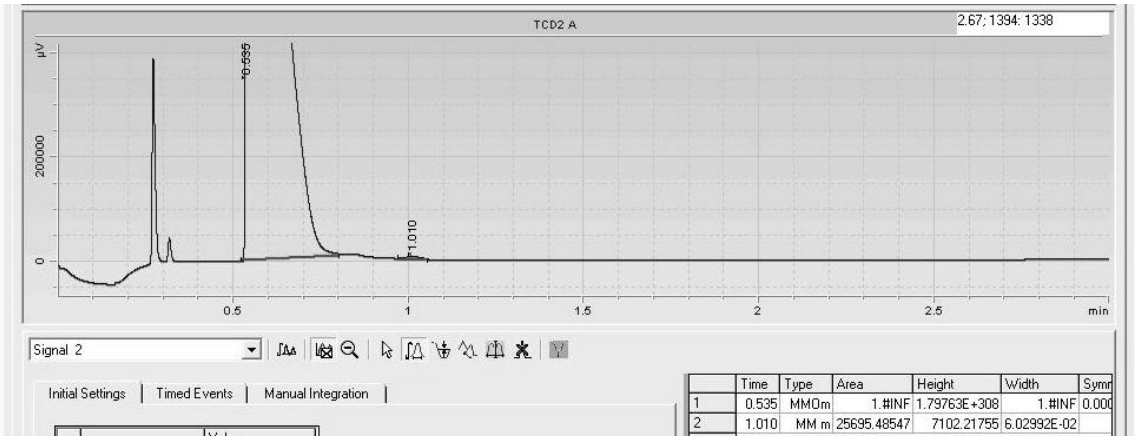

Figure 6.24 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -2.4 V vs. Ag/Ag$^+$, at a temperature of 45ºC, at a pressure of 63.3 bar and 2 hours reaction time (reaction 11).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.535 min), and a peak to identify with a new injection of bottle calibration (tr = 1.010 min)

Reaction 12

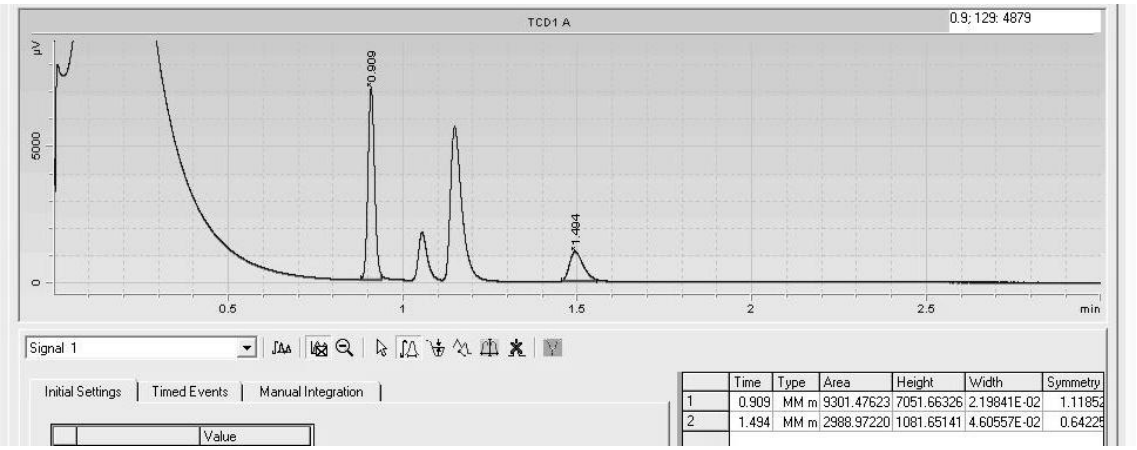

Figure 6.25 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 62.9 bar and 30 minutes reaction time (reaction 12).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.909 min) and methane (tr = 1.494 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

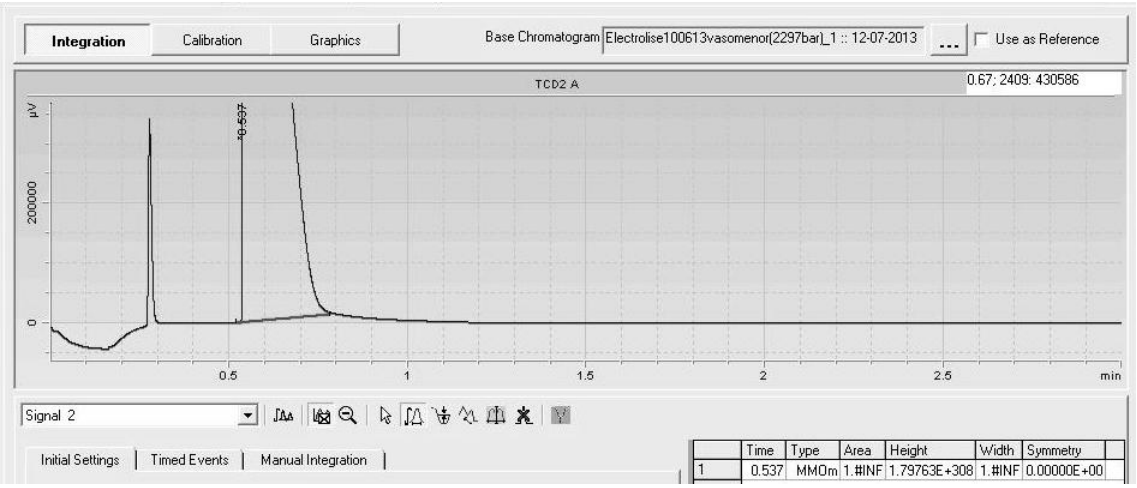

Figure 6.26 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 62.9 bar and 30 minutes reaction time (reaction 12).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.537 min).

Annex 6 – Chromatograms of the reactions with the carbon electrode

Reaction 13

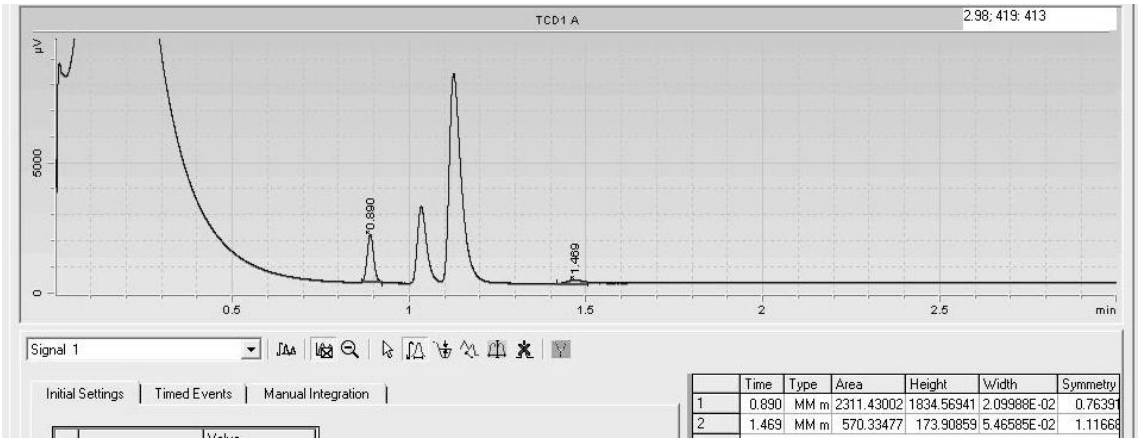

Figure 6.27 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 63.6 bar and 1 hour reaction time (reaction 13).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.890 min) and methane (tr = 1.469 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

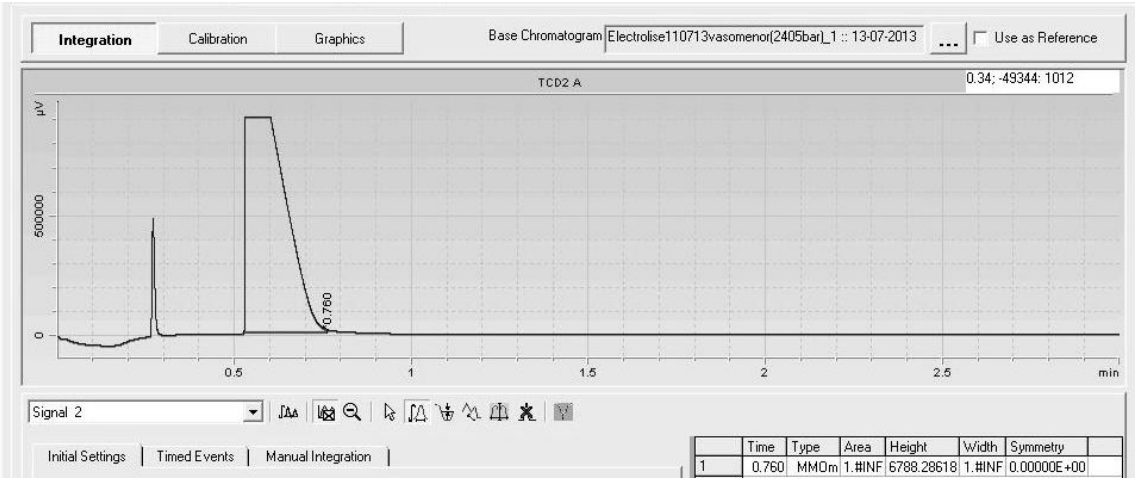

Figure 6.28 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, pressure of 63.6 bar and 1 hour reaction time (reaction 13).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.760 min).

Reaction 14

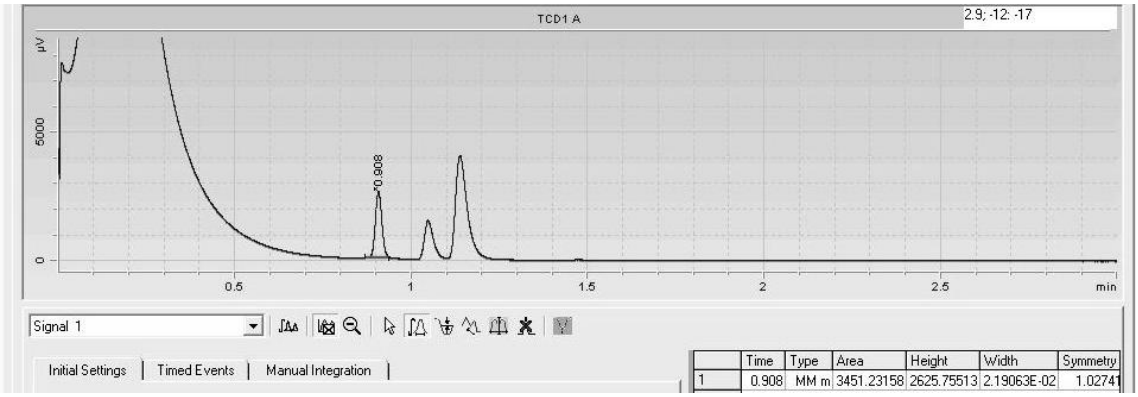

Figure 6.29 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85.3 bar and 1 hour reaction time (reaction 14).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.908 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

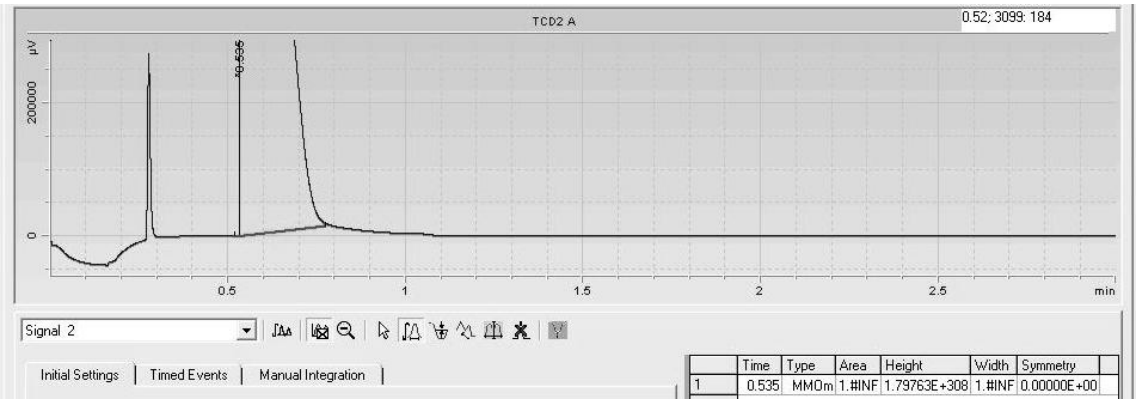

Figure 6.30 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 85.3 bar and 1 hour reaction time (reaction 14).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.535 min).

Reaction 15

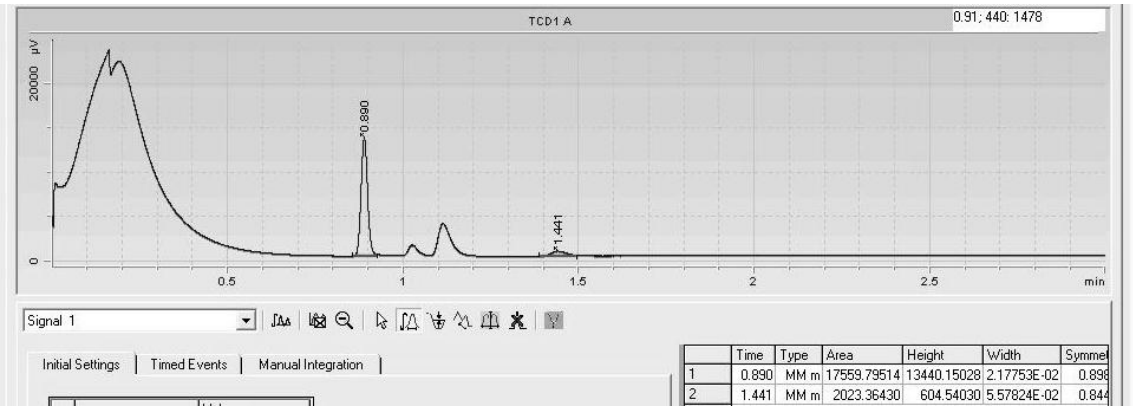

Figure 6.31 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -2.4 V vs. Ag/Ag$^+$, at a temperature of 45ºC, at a pressure of 62.5 bar and 1 hour reaction time (reaction 15).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.890 min) and methane (tr = 1.441 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

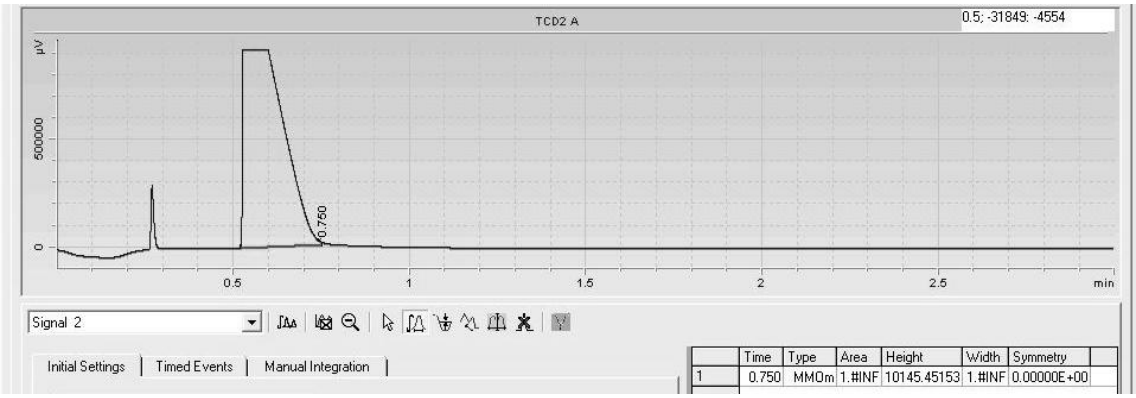

Figure 6.32 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -2.4 V vs. Ag/Ag$^+$, at a temperature of 45ºC, at a pressure of 62.5 bar and 1 hour reaction time (reaction 15).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.750 min).

Reaction 16

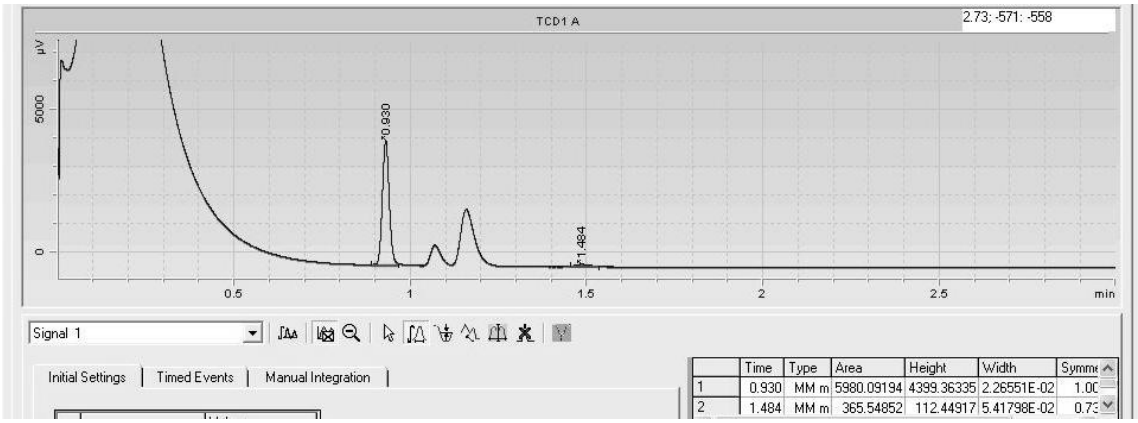

Figure 6.33 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -2.4 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 84.7 bar and 3 hours reaction time (reaction 16).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.930 min) and methane (tr = 1.484 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

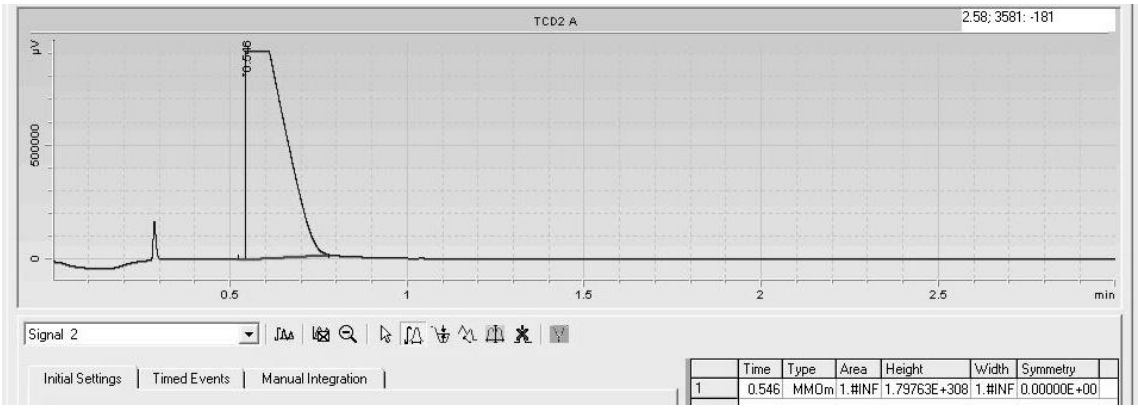

Figure 6.34 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -2.4 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 84.7 bar and 3 hours reaction time (reaction 16).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.546 min).

Annex 7 – Chromatograms of the reactions with the Nanoparticles of copper and nickel

Reaction 17

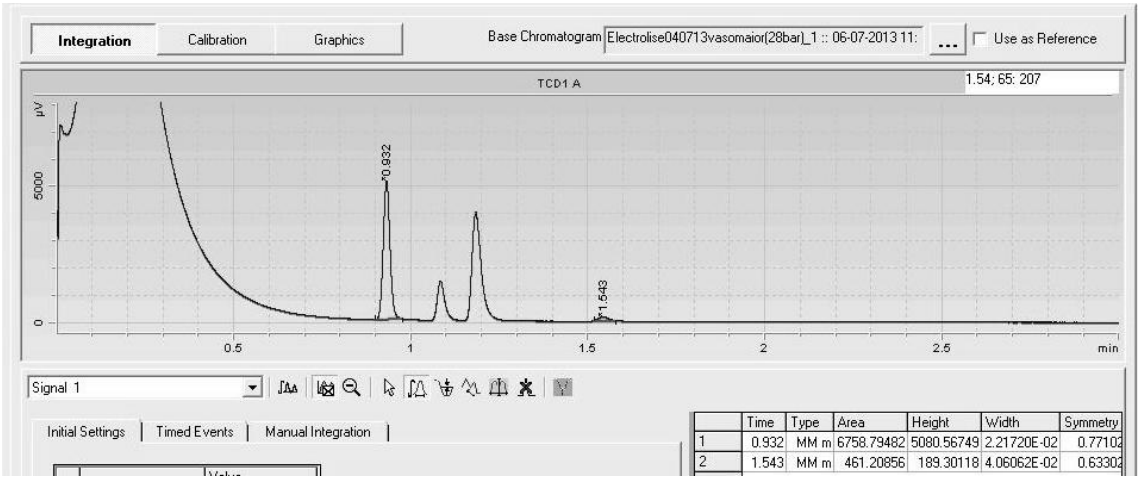

Figure 6.35 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 64.1 bar and 30 minutes reaction time (reaction 17).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.932 min) and methane (tr = 1.543 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

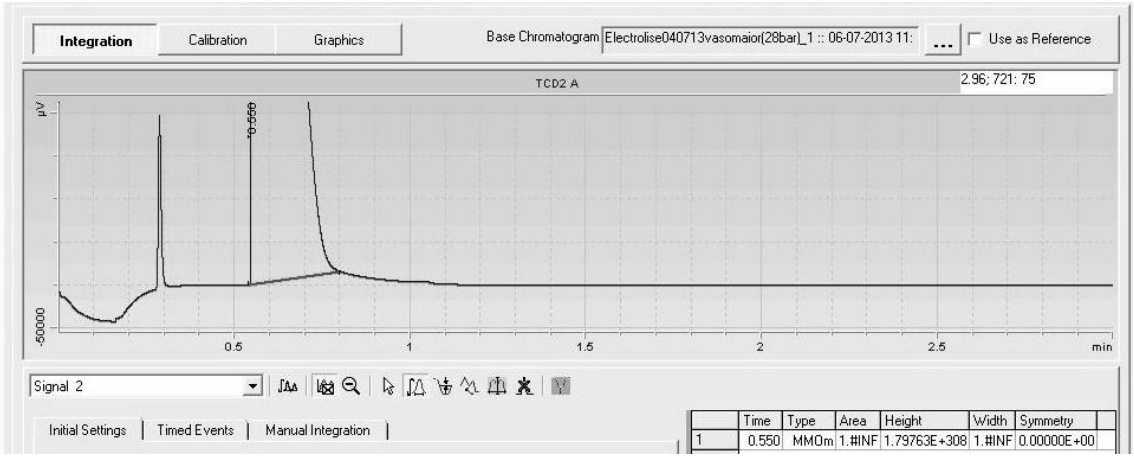

Figure 6.36 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 64.1 bar and 30 minutes reaction time (reaction 17).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.550 min).

Reaction 18

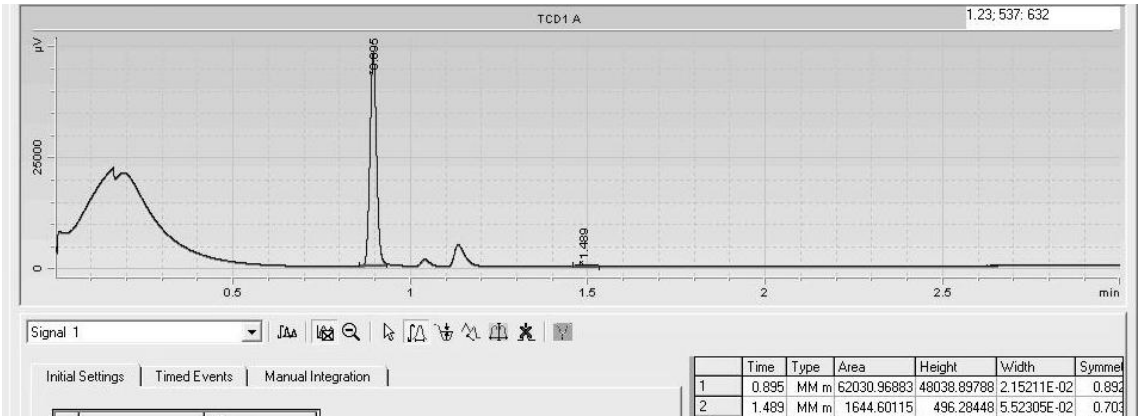

Figure 6.37 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 62.5 bar and 1 hour reaction time (reaction 18).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.985 min) and methane (tr = 1.489 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

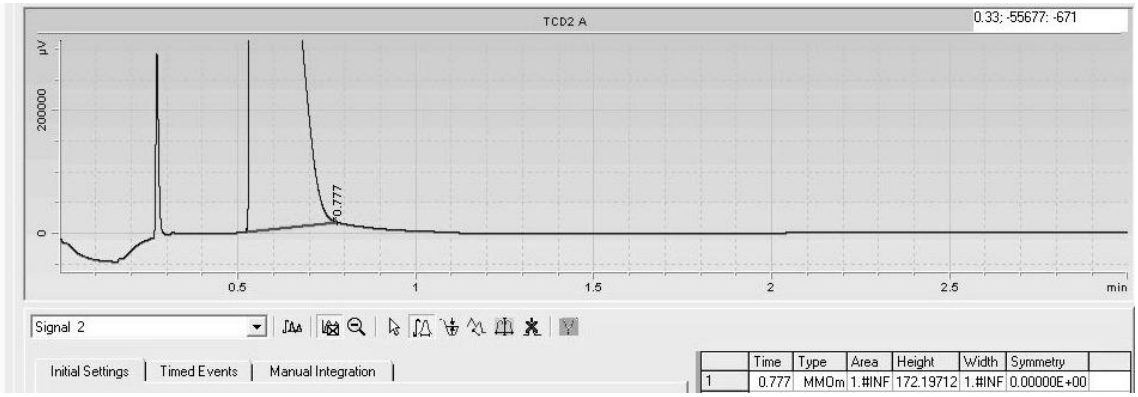

Figure 6.38 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag^+, at a temperature of 45ºC, at a pressure of 62.5 bar and 1 hour reaction time (reaction 18).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.777 min).

Reaction 19

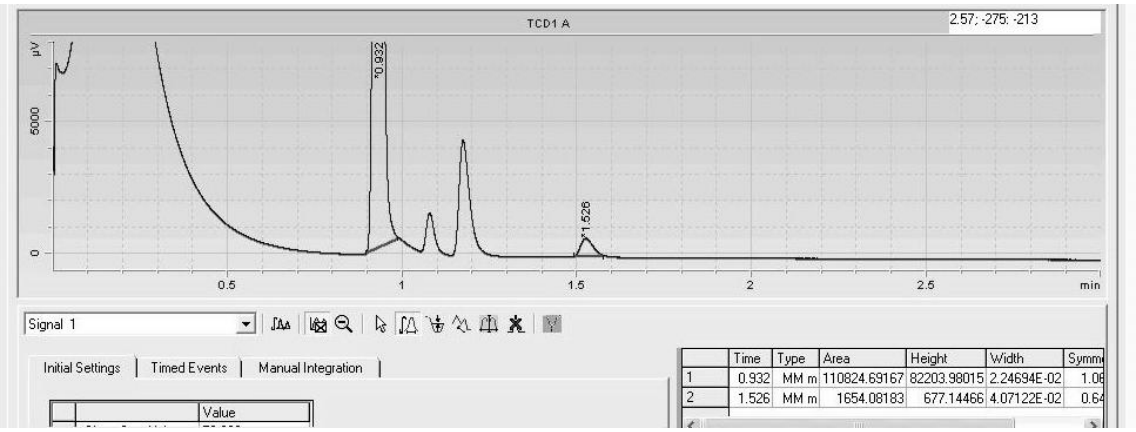

Figure 6.39 – Channel 1 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag$^+$, at a temperature of 45ºC, at a pressure of 66.3 bar and 1 hour reaction time (reaction 19).

In the Channel 1, it is possible observe the peak referent to hydrogen (tr = 0.932 min) and methane (tr = 1.526 min). Concentrations were calculated according to the following areas of calibration: CH_4=3486 e H_2=29912.7

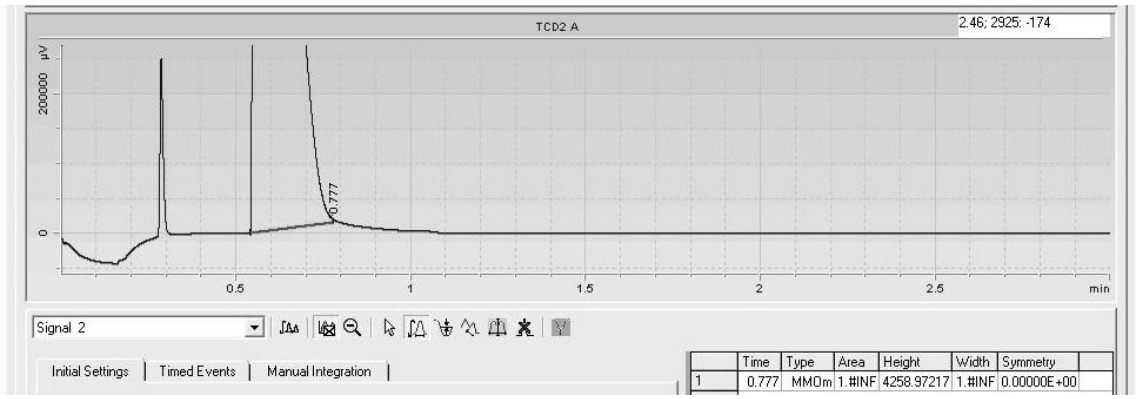

Figure 6.40 – Channel 2 of the gas chromatogram of CO_2 electrolysis carried out with an applied potential at -1.8 V vs. Ag/Ag$^+$, at a temperature of 45ºC, at a pressure of 66.3 bar and 1 hour reaction time (reaction 19).

In the Channel 2, it is possible observe the peak referent to CO_2 (tr = 0.777 min).

Annex 8 – Electrolysis (Faradaic Efficiency)

Reaction 2

With the program used to carry out the electrolysis, we can obtain the current that pass over the time. The figure below shows the curve of the current vs. time:

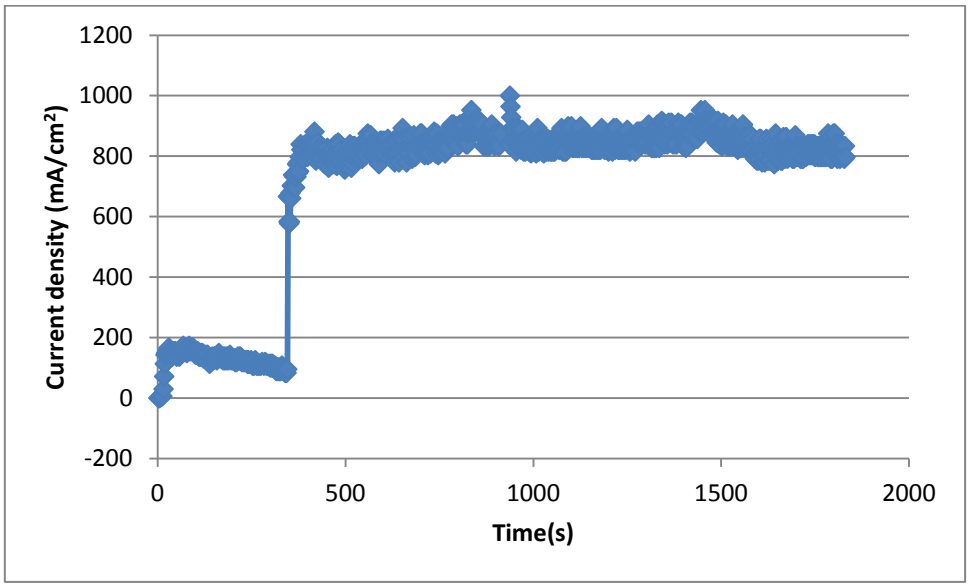

Figure 6.41 – Curve carried out with the programme CONTROL. With a potential at -1.8 V vs. Ag/Ag^+, at a pressure of 66.5 bar and 30 minutes reaction time.

This data-allows the calculation of the total charge passed during the electrolysis. It was obtained a charge of 2168 C. From the concentration for every compound obtained by GC, and the conditions of the several parts of the facility like temperature and pressure, it is possible calculate the theoretical charge for any compound formed during the electrolysis. So, the theoretical charge for the methane and hydrogen were the following:

CH_4 = 469 C;

H_2 incorporated into the CH_4 = 235 C

H_2 detected = 1537 C

So, using the equation shown in section 1.3.2, the faradaic efficiency for these compounds was:

FE (CH_4) = 22%

FE (H_2 incorporated) = 11%

FE (H_2 detected) = 71%

Total current (CH_4+H_2) = 104%

This means that no other compound was formed in this electrolysis experiment.